A TEXT-BOOK
OF
INORGANIC CHEMISTRY

RICHTER

RICHTER'S CHEMISTRIES

AUTHORIZED TRANSLATIONS

BY EDGAR F. SMITH, M.A., PH.D., SC.D.

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF PENNSYLVANIA; MEMBER OF THE CHEMICAL SOCIETY OF BERLIN, AMERICAN PHILOSOPHICAL SOCIETY, ETC., ETC.

Professor Richter's methods of arrangement and teaching have proved their superiority by the large sale of his books throughout Europe and America, translations having been made in Russia, Holland, and Italy. The success attending their publication in this country could only have been attained for good books that have been found useful, practical, and thoroughly up to the times.

The Chemistry of the Carbon Compounds, or Organic Chemistry

Third American, translated from the Eighth German Edition by PROF. R. ANSCHÜTZ, University of Bonn. Thoroughly Revised, Enlarged, and in many parts Rewritten. Illustrated. Two Volumes.

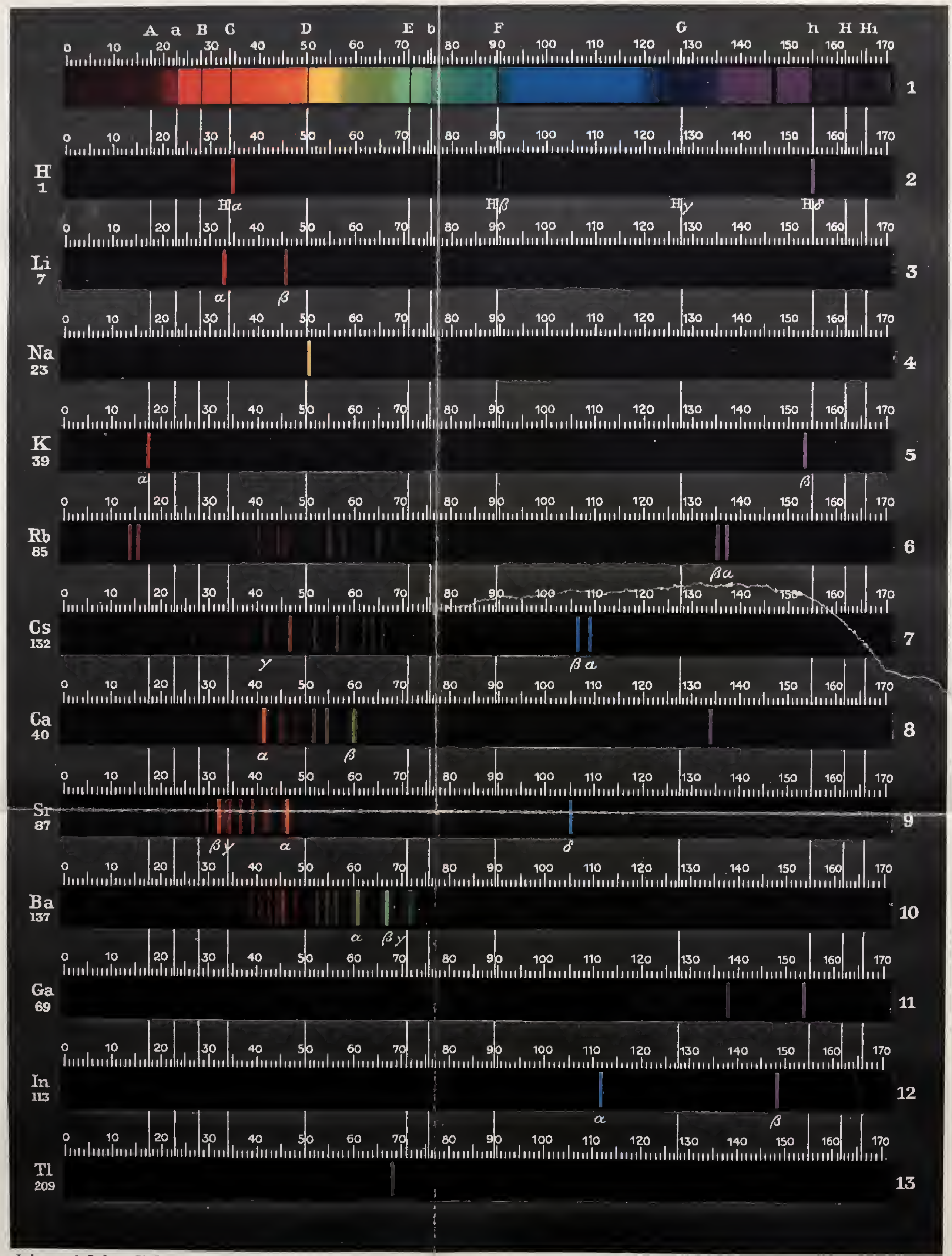
Vol. I.	Aliphatic Series. 625 pages.	Cloth, net, $3.00
Vol. II.	Carbocyclic and Heterocyclic Series. 671 pages.	Cloth, net, $3.00

INORGANIC CHEMISTRY

Fifth American from the Tenth German Edition by PROF. H. KLINGER, University of Königsberg. Thoroughly Revised and in many parts Rewritten. With many Illustrations and Colored Plate of Spectra. Cloth, net, $1.75

⁂ *Special Catalogues of Books on Chemistry, Hygiene, Pharmacy, Medicine, Dentistry, and Nursing sent free upon application. Correspondence solicited.*

P. BLAKISTON'S SON & CO., PUBLISHERS
PHILADELPHIA



Lehman & Bolton, Phila,

Philadelphia, P. Blakiston's Son & Co.

VICTOR VON RICHTER'S

TEXT-BOOK
OF
INORGANIC CHEMISTRY

EDITED BY
PROF. H. KLINGER
UNIVERSITY OF KOENIGSBERG

AUTHORIZED TRANSLATION
BY
EDGAR F. SMITH
PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA

(ASSISTED BY WALTER T. TAGGART)
INSTRUCTOR IN CHEMISTRY

Fifth American from the Tenth German Edition

CAREFULLY REVISED AND CORRECTED

WITH SIXTY-EIGHT ILLUSTRATIONS ON WOOD
AND
COLORED LITHOGRAPHIC PLATE OF SPECTRA

PHILADELPHIA
P. BLAKISTON'S SON & CO.
1012 WALNUT STREET
1900

WM. F. FELL & CO.,
ELECTROTYPERS AND PRINTERS,
1220-24 SANSOM STREET,
PHILADELPHIA.

PREFACE

TO THE

FIFTH AMERICAN EDITION.

The student of the present edition will discover that it differs very materially from all preceding editions. This is largely due to the fact that the editor has endeavored to give due consideration to the more recent, well-established discoveries in chemical science; hence additions will be found relating to the general properties and the measurement of gases, to the atmosphere and the interesting constituents lately observed in it, to the theory of dilute solutions and electrolytic dissociation, to the electrolysis of salts, to alloys, etc. Thus revised, it is hoped that the book will continue to occupy the position it has so long held among works devoted to the inorganic portion of chemical science.

The translator would take this opportunity to acknowledge his great indebtedness and to return his sincere thanks to Mr. Walter T. Taggart, upon whom devolved the task of arranging the crude manuscript for the press and the revision of the proof-sheets.

The John Harrison
Laboratory of Chemistry.

PREFACE

TO THE

FIRST AMERICAN EDITION.

The success of PROF. VON RICHTER'S work abroad would indicate its possession of more than ordinary merit. This we believe true, inasmuch as, in presenting his subject to the student, the author has made it a point to bring out prominently the relations existing between fact and theory. These, as well known, are, in most text-books upon inorganic chemistry, considered apart, as if having little in common. The results attained by the latter method are generally unsatisfactory. The first course—that adopted by our author—to most minds would be the more rational. To have experiments accurately described and carefully performed, with a view of drawing conclusions from the same and proving the intimate connection between their results and the theories based upon them, is obviously preferable to their separate study, especially when they are treated in widely removed sections or chapters of the same book. Judging from the great demand for VON RICHTER'S work, occasioning the rapid appearance of three editions, the common verdict would seem to be unanimously in favor of its inductive methods.

In the third edition, of which the present is a translation, the Periodic System of the Elements, as announced by MENDELEJEFF and LOTHAR MEYER, is somewhat different, in the manner of development and presentation, from that appearing in the previous editions. This was done to give more prominence to and make more general the interesting relations disclosed by it. Persons examining this system carefully will be surprised to discover what a valuable aid it really has been, and is yet, in chemical studies. Through it we are continually arriving at new relations and facts, so that we cannot well hesitate any longer in adopting it into works of this character. It is, indeed, made the basis of the present volume. In accordance with it, some change in the treatment of the metals, ordinarily arbitrarily considered, has been made.

A new feature of the work, and one essentially enlarging it, is the introduction of the thermo-chemical phenomena, briefly presented in the individual groups of the elements and in separate chapters, together with the chemical affinity relations and the law of periodicity. "Hereby more importance is attributed to the principle of the greatest heat development than at present appears to belong to it, because it was desired, from didactic considerations, by the explanation of the few anomalies, to afford the student the incentive and opportunity of deductively obtaining the majority of facts from the thermal numbers, on the basis of a simple principle. To facilitate matters, there is appended to the volume a table containing the heat of formation of the most important compounds of the metals."

Trusting that the teachings of this work will receive a hearty welcome in this country, and that they will meet a want felt and often expressed by students and teachers, we submit the following translation of the same.

TABLE OF CONTENTS.

INTRODUCTION.

HYDROGEN AND THE NON-METALS.

THE METALS.

A TEXT-BOOK

OF

INORGANIC CHEMISTRY.

INTRODUCTION.

The natural sciences are occupied with the investigation of the innumerable substances and changes by which we are surrounded. Physics and chemistry differ in a sense from the other sciences, in that their domain of research is not restricted to any very definite province of nature; indeed, it is not confined to any one planet. This is due to the fact that all changes, so far as they are perceptible to our senses, are referable to chemical and physical causes. The best and most satisfactory information relative to the properties and composition of a substance, no matter what its source, is afforded by physics and chemistry. For these reasons, therefore, these two sciences—chemistry and physics—are regarded as the *general* natural sciences in contradistinction to the other more *special* sciences.

Physics deals with the doctrine of equilibrium and with that of motions. The latter are visible, as those of mass—in fall, projection, rotation, propagation in a plane, etc.; or they are invisible, and are only perceptible by their results—sound, heat, light, electricity. Chemistry, on the other hand, reveals to us the composition of matter, and, in the formation of new compounds, acquaints us with the rules and laws by which its various forms act upon each other. The domain of chemistry and physics consequently extends throughout all the natural kingdoms, and each of the *special* natural sciences, even astronomy, avails itself of the aid given by physics and chemistry to attain its own particular goal. However, these two sciences are mutually dependent upon one another for, so far as we know, there cannot be motion without matter, nor matter without motion.

The influence exerted by chemistry and physics upon civilization corresponds to their exalted position in the group of natural sciences. By means of these sister sciences the products and forces of nature have been more completely utilized than ever before, hence there are but few fields of human activity which in the course of the present century have not been enriched by the accumulation of chemical and physical observations. If the conquests of chemical and physical investigation of even the last five years were suddenly to disappear an almost unbearable retrogression would be felt in commerce, manufacture, the various industries and in agriculture, and every individual would find himself having recourse to innumerable advantages and facilities of which at present he is scarcely conscious.

The following figures give some idea of the importance of German chemical industries. In 1895, 114,581 operators were engaged in 5974 factories devoted to chemical manufacture; these represented in round numbers 100,000,000 M. or $25,000,000 in wages, etc. The exports of chemical products for the same year were valued at 290,000,000 M. or $72,500,000.

Compare: Wickelhaus, Wirthschaftliche Bedeutung chemischer Arbeit, Berlin, 1893; Ferd. Fischer, Das Studium der technischen Chemie, Braunschweig, 1897.

A closer scrutiny of natural objects discloses the fact that they in time succumb to many more or less serious alterations or changes. Although no abrupt boundaries are presented in nature, but gradual transitions and intermediate steps throughout, two tolerably distinct classes of phenomena may be observed. Some changes in the condition of bodies are only superficial (external), and are not accompanied by material alteration in substance. Thus heat converts water into steam, which upon subsequent cooling is again condensed to water, and at lower temperatures becomes ice. In these three conditions, the solid, liquid, and gaseous, the *substance* or the *matter* of water or ice is unchanged; only the separation and the motion of the smallest particles—their states of aggregation—are different. If we rub a glass rod with a piece of cloth, the glass acquires the property of attracting light objects, *e. g.*, particles of paper. It becomes electrified. An iron rod allowed to remain suspended vertically for some time slowly acquires the power of attracting small pieces of iron. Through the earth's magnetism it has become magnetic. In both instances the glass and iron receive new properties; in all other respects, in their external and internal form or condition, they have suffered no perceptible alteration; the glass is glass, and the iron remains iron. All such changes in the condition of bodies, unaccompanied by any real alteration in substance, are known as *physical phenomena*.

Let us now turn our attention to the consideration of another class of phenomena. It is well known that ordinary iron undergoes a change, which we term *rusting*, *i. e.*, it is transformed into a brown substance which is entirely different from iron. On mixing finely divided copper filings with flowers of sulphur (pulverulent sulphur) there results an apparently uniform, grayish-green powder. If this be examined, however, under a magnifying glass, we can very plainly distinguish the red metallic copper particles in it from the yellow of the sulphur; by treating with water, the specifically lighter sulphur particles can easily be separated from those of the copper. Carbon bisulphide will dissolve out the sulphur particles. Hence this powder represents nothing more than a *mechanical mixture*. If, however, this mixture be heated, *e. g.*, in a glass test-tube, it will commence to glow, and on cooling, a black, fused mass remains, which differs in all respects from copper and sulphur, and even under the strongest microscope does not reveal the slightest trace of the latter, and elutriation with water or treating with carbon bisulphide will not affect a separation of the ingredients. By the mutual action of sulphur and copper in presence of heat, a new body with entirely different properties has been produced, and is named copper sulphide. Mixtures of sulphur with iron or with other metals act in a similar manner; the resulting bodies are known as sulphides.

Such mutual action of different bodies occurs not only under the influence of heat, but frequently at ordinary temperatures. If, *e.g.*, mercury and sulphur are rubbed together in a mortar, there is produced a uniform, black compound, called mercury sulphide. The action of gaseous chlorine upon various metals is quite energetic. When finely divided antimony is shaken into a flask filled with yellow chlorine gas, flame is produced; each antimony particle burns in the chlorine with a bright white light. The product of this action of solid metallic antimony and gaseous yellow chlorine is a colorless, oily liquid, known as antimony chloride. Such occurrences, therefore, in which a complete and entire alteration takes place in the bodies entering the reaction, are termed *chemical phenomena.*

In the previously described experiments we observed the phenomena of *chemical combination;* from two different bodies arose new homogeneous ones. The opposite may occur: the *decomposition* of compound bodies into two or more *dissimilar* ones. If red mercuric oxide be heated in a test-tube, it will disappear; a gas (oxygen) is liberated, which will inflame a mere spark on wood; in addition, we find deposited upon the upper, cooler portions of the tube, globules of mercury. From this we observe that on heating solid red mercuric oxide two different bodies arise: gaseous oxygen and liquid mercury. We conclude, then, that mercuric oxide holds in itself, or consists of, two constituents—oxygen and mercury. This conclusion, arrived at by decomposition, or *analysis,* may be readily verified by combination or *synthesis.* It is only necessary to heat mercury for some time, at a somewhat lower temperature than in the preceding experiment, in an atmosphere of oxygen, to have it absorb the latter and yield the compound we first used—red mercuric oxide. The direct decomposition of a compound body into its constituents by mere heat does not often happen. Generally, the cooperation of a second substance is required, which will combine with one of the constituents and set the other free. In this manner we can, for example, effect the decomposition of the previously synthesized mercury sulphide, viz., by heating it with iron filings; the iron unites with the sulphur of the mercury sulphide, to form iron sulphide, while the mercury is set free.

If, in a similar manner, natural objects be decomposed, bodies or substances are finally reached which have withstood all attempts to bring about their division into further constituents, and which cannot be formed by the union of others. Such substances are *chemical elements;* they cannot be converted into one another, but constitute, as it were, the limit of chemical change. Their number, at present, is about 70; some have been only recently discovered. To them belong all the metals, of which iron, copper, lead, silver, and gold are examples. Other elements do not possess a metallic appearance, and are known as *metalloids* (from εἴδω, I resemble). It would be more correct to term them *non-metals.* To these belong sulphur, carbon, phosphorus, oxygen, etc. The line between metals and non-metals is not very marked. Thus, mercury, despite the fact that it is liquid at the ordinary temperature, must be included among the metals because of its chemical properties.

All the substances known to us are made up of these elements. Water is a compound of two gaseous elements—hydrogen and oxygen ; common salt consists of the metal sodium and the gas chlorine. The elements make up not only our own earth, but the heavenly bodies are composed of them ; at least as far as has been proved by spectrum analysis.

THE PRINCIPLE OF THE INDESTRUCTIBILITY OF MATTER.

If the total weight of substances, which are to act chemically upon one another, be determined, and the chemical action be then allowed to occur, it will be discovered upon ascertaining the weight of the resulting bodies, if due consideration be given for unavoidable errors of experiment, that no loss or increase in weight has occurred—no change in mass, because mass and weight are strictly proportional to each other for one and the same place. It is in these cases immaterial whether a compound body be resolved into its elements, or whether elements unite to produce compound bodies; the products present after the chemical reaction will always weigh exactly what the bodies preceding the reaction weighed (compare the experiments of Landolt, Ber. **26** (1893), 1820). Well-known, general phenomena apparently contradict this scientific conclusion. We observe plants springing from a small germ and constantly acquiring weight and volume. This spontaneous increase of substance, however, is only seeming. Closer inspection proves conclusively that the growth of plants occurs only in consequence of the absorption of substance from the earth and atmosphere. The opposite phenomenon is seen in the burning of combustible substances, where an apparent annihilation of matter takes place. But even in this, careful observation will discover that the combustion phenomena consist purely in a transformation of visible solid or liquid bodies into non-visible gases. Carbon and hydrogen, the usual constituents of combustible substances, *e. g.*, petroleum or wood, combine in their combustion with the oxygen of the air and yield gaseous products—the so-called carbon dioxide and water—which diffuse into the atmosphere. If these products be collected, their weight will be found not less, but indeed greater, than that of the consumed body, and this is explained by the fact that in addition to the original weight they have had the oxygen of the air added. Such a combustion must, therefore, be regarded as a conversion of visible solid or liquid substances into invisible gaseous matter.

The production (creation) or annihilation of matter has never been demonstrated as occurring in any change. A compound body is composed of certain elements, and contains a very definite quantity by weight of each of them. If it decompose it naturally breaks down into its constituents, which perhaps reunite in some other manner to form new compounds, always, however, preserving their original nature, their original weight and their masses. This fundamental truth is *the law of the indestructibility of matter.* The early Grecian philosophers arrived at this conclusion by a keen observation of the changes of daily life (compare

Lucretius—"Nature"), and since that time it has always been viewed as an established fundamental principle of exact, scientific investigation. Consult Debus, Ueber einige Fundamental-Sätze der Chemie, Kassel, 1894.

THE PRINCIPLE OF THE CONSERVATION OF ENERGY.

All imaginable, appreciable, natural phenomena have their causes, which escape simple observation, and are only realized by scientific research. We observe that iron rusts on exposure to the air. By chemical investigation we learn that rust is a compound of iron and oxygen. This latter, as we also learn from chemistry, is a constituent of the air. If it be removed from the latter, the iron will cease to rust. Hence the tendency of iron and oxygen to combine with one another is designated as the cause of the rusting. It is generally said that a force exists between them, which effects their union and this force is called chemical affinity. In changes of other kinds our explanation assumes the presence of some force. The falling of bodies is attributed to the force of gravitation—a universal attracting force, which even influences the course of the stars. The decomposition of a body by external efforts acts in opposition to its cohesive force. Two different bodies directly in contact with one another are held together by the adhesive force existing between them. By assumptions similar to these it is possible to refer an almost infinite number of changes to but comparatively few causes. But, in doing this, it must be remembered that the nature of the force continues enigmatical, even if we know the laws, by which it acts, as well as we know those of gravity.

At present the movements of the parts of matter are considered to be the cause of other phenomena which formerly were ascribed to the actions of special forces. It has long been known that a sounding body completes certain vibrations, which are imparted to the surrounding air and arrive thereby to the tympana of our ears. The same is true of the phenomena of light and heat. It is supposed that the heat phenomena are due to an energetic oscillating motion of the smallest particles of a body. Upon grasping a warm substance, motion present in it is partially transferred to us and we experience warmth. If, on the contrary, heat motion be passed from the hand to the object touched, the latter appears to us to be cold. At sufficiently elevated temperatures, and indeed even under other conditions (phosphorescence, fluorescence) the heat motions of bodies produce in the surrounding æther (a hypothetical medium, enigmatical in its nature and capable of penetrating everything) motion extending in all directions in a wave-like manner and known as *radiant heat*. If these waves follow each other rapidly enough they become *light waves* and are perceived as such by the retina of the eye. The source of electric phenomena and of the x or Röntgen rays is also supposed to be due to motion, of an unexplained nature, present in the æther. H. Hertz in 1888 demonstrated by the radiation of a periodic electric force reversing its direction that these rays were subject to the same laws as those of light and radiant heat. They are not only propagated in direct lines with all the velocity of light but are similarly reflected and refracted. Consequently, in the periodic change of direction we find the same motion alterations of the æther to be at the basis of light and radiant heat, as they are the cause of electric phenomena.

Numerous physical investigations have demonstrated that the various forms of motion can be transferred not only from one body to another but that they can be converted into one another. The bullet which in its flight is sustained by resistance becomes hot; the visible motion of the entire mass ceases and is then converted into the invisible motion of the minutest particles perceptible to us as heat. Conversely, the motion of the smallest particles is changed to that of large masses, if by means of the steam engine we produce driving force by heat, and the latter by combustion, a chemical change.

It will be discovered upon attempting to measure these changes that the different forces or modes of motion bear a fixed ratio of transformation to one another. According to the proposition, *causa æquat effectum*, they are subject to equivalent convertibility. At present the indestructible portion of all these changes is termed *energy*, which manifests itself as (1) *mechanical energy*, (2) *thermal energy*, (3) *electric* and *magnetic energy*, (4) *chemical* and *internal energy* and (5) *radiant energy*.

The power of a body to do work is called *energy*. It is distinguished as potential and kinetic. Examples are as follows: The mass m, acted upon by the constant force p, traverses the distance s and acquires the speed v. This would be represented by the equation $ps = \frac{m}{2} v^2$. As the force p has acted through the distance s, it has performed the work ps. If a hammer, weighing p, be raised to the height s, the work done, opposed to gravity, equals ps. This work is present as *potential energy* in the raised hammer, so far as the presence of a force and its removal through space can possibly make a mechanical action present. If the hammer be allowed to fall it acquires *kinetic energy* $\frac{m}{2} v^2$ (active force), which is equal to the work expended in raising the hammer, or the potential energy of the raised hammer. In the fall the potential is transformed into kinetic energy (κινέω—to move; ἐνεργέω—to act).

A given mass-motion can be converted into a definite heat-quantity. By the application of the latter, work can be performed again equivalent to the mass-motion (first principle of the mechanical theory of heat). The quantity of heat sufficient to raise 1 kilogram of water at the ordinary temperature 1° C. is taken as the unit in the determination of heat and is called *calorie* (large). To produce this unit by mass-motion would require mechanical work (at the average geographical latitude) equal to 426 kilogram-meters. This quantity signifies that if under the conditions mentioned as to place 1 kilogram falls through 426 meters, or 426 kilograms through 1 meter, and the resulting total kinetic energy be transformed into heat, the latter will raise 1 kilogram of water from 15° to 16° in temperature. In the conversion of heat into mass-motion, however, one calorie will disappear for every 426 kilogram-meters of work performed. This magnitude (or constant) is known as the *mechanical equivalent of heat*.

Chemical energy can be measured by the heat or electricity developed in chemical changes. While all forms of energy can be converted without difficulty into heat, this particular form is only altered with limitations into the other forms. It is only when heat passes from a warmer to a colder substance that a definite portion of it can by proper appliances be changed into mechanical work. Could this so occur that the greatest possible portion of the heat could be utilized in the performance of mechanical work, then the process might be reversed. If, however, the greatest possible quantity of heat is not consumed in doing such work but is lost by conduction and radiation from a higher to lower temperature, then the change is not reversible. For a portion, at least, of the heat there is no possibility of change to mechanical work; it is permanently lost (*degradation of energy*). The reversibility is made impossible by such changes (conduction, radiation, friction, etc.), which take place under given conditions, of their own accord. As the opposite conversions do not occur spontaneously (the passage of heat from a body of lower to one of higher temperature), in nature the changes of the first order must exceed those of the second order. The sum of all the conversion-values (calculated as proceeding positively in the sense of the first group) is termed *entropy* (*τροπὴ*—conversion). The entropy of all nature is therefore in the act of constant increase (Clausius, Second Principle of the Mechanical Theory of Heat).

The law of the conservation of energy, according to which the energy in nature is of a convertible character but unalterable in quantity, constitutes one of the most important foundations of the science of nature.

It was first clearly explained and definitely enunciated by Julius Robert Mayer (1842), a physician of Heilbronn (Annalen, 42, 233; see also his "Mechanik der Wärme gesammelte Schriften"). Not knowing of Mayer's work, or of the treatise of Colding (1843), a Dane, in which the principle of energy was also developed, Hermann v. Helmholtz (1847) announced the law as empirical, followed and developed it mathematically through all the domains of natural phenomena (Ueber die Erhaltung der Kraft, Berlin, 1847). Mayer was also the first to discover the mechanical equivalent of heat, which shortly afterwards James Prescott Joule definitely determined by accurate experiments.

Heat almost invariably appears in chemical union; even light and electricity can be produced by chemical processes, or work can be performed in opposition to external pressure by increase in volume. All these forms of energy owe their origin to the potential energy of the chemical forces, which in the process of chemical change do work. Hence, we may speak of *chemical energy* or of *chemical tension.* In the chemical decomposition of a compound body into its components, on the other hand, heat is usually absorbed and disappears as such and becomes chemical energy. Thus, in the union of approximately 1 kilogram of hydrogen with 8 kilograms of oxygen to produce 9 kilograms of water a quantity of heat, equivalent to 34,200 calories, is set free, and this corresponds to work equivalent to $34,200 \times 426 = 14,569,200$ kilogram-meters. In the decomposition, on the other hand, of 9 kilograms of water into hydrogen and oxygen, the same force or quantity of heat is necessary. Therefore, the same quantity of force or motion must be contained in the form of chemical energy in the liberated hydrogen and oxygen.

Although all bodies, and the elements especially, possess chemical energy, they do not manifest it in the same way. Some of them react readily with one another and others with difficulty or not at all. The cause of this variation in behavior is entirely unknown to us. It is customary to express the fact by saying the bodies have a strong, a feeble, or no *affinity* for one another. Formerly, bodies which combined chemically, were supposed to be related to each other, and it was assumed that their affinity—their tendency toward one another—was satisfied by their union. This choice of terms was unfortunate. The nature of the chemical attraction, which produces and holds chemical compounds together is just as enigmatical as that of gravity. Even the laws in accordance with which affinity acts are scarcely known to us. It is only in recent times that advances have been made in this direction, since the positions and the motions of atoms and of molecules have been regarded as affording hints as to the cause of a reaction.

CONSTITUTION OF MATTER.

26

ATOM AND MOLECULE.

If we seek to give expression to the constitution of the chemical elements and the bodies composed of them we return, if guided by experience, to the ancient atomic hypothesis which alone is justified by the present condition of chemical and physical investigation. It appears that the Indian and Grecian natural philosophers established this same hypothesis in a purely inductive manner [Kanāda (founder of the Vaiśeshika system), Lucippus, Democritus (500 B. C.) and Epicurus (400 B. C.)].

The foundation of this hypothesis is brilliantly set forth in the first book of Lucretius (died 55 B. C.) "Ueber die Natur der Dinge." Numerous observations are recorded. The following occurs there in substance: All bodies can be divided into infinitely small parts, no longer recognizable by sight or taste. Invisible aqueous vapor separates from the air as water upon cold objects and again disappears on the approach of heat. The ring that is constantly worn on the finger becomes thinner in the course of years. Dropping water wears away the stone. The smooth pavement is made rough by walking. All these things occur without our perceiving what at any one time departs from the ring, etc. Hence we conclude the bodies are composed of invisible, extremely small parts, which to us are without mass. These particles, the atoms (ἄτομος—indivisible), are indestructible and cannot be created. There is nothing beyond them and the vacant space between. The difference in things is due to the difference in number, size, form, and arrangement of the atoms. There is no qualitative difference in the atoms, they act upon one another only by contact and pressure. Change is only a union and separation of atoms; nothing occurs by chance but everything by reason and with necessity. Thus far Lucretius.

In the first half of the 17th century the atomic idea, which until then had been driven into the background by the Aristotelian philosophy, was resuscitated by Daniel Sennert, a German physician, and a French ecclesiastic named Pierre Gassendi. They adopted the Greek atomic doctrine; and, from the point of view of the atomists, constitute the connecting link between the past and the present. Since, however, our modern atomic notions have developed step by step from the ideas of Sennert and Gassendi, their beginnings go back to and have their origin in Lucippus and Democritus. Atoms were introduced into chemistry by Robert Boyle, a contemporary and follower of Gassendi. Boyle was the first chemist to devote his experiments to the noble purpose of investigating nature. (Compare F. A. Lange, Geschichte des Materialismus, 3 Aufl. 1876; Griesbach physik.-chem. Propädeutik (1895), and the fasciculus of Debus referred to on page 21.)

The scientific foundations of our present atomic doctrine will be described later. Its fundamental ideas alone will be given now. We assume that an element consists of atoms perfectly similar to one another, but differing from those of other elements. We must grant that there are as many kinds of atoms as there are different elements. A compound body like iron sulphide, according to this view, is produced by the combination of sulphur atoms with iron atoms in a definite ratio. Those particles of a compound, representing the limit of divisibility so far as similarity goes, are called molecules (*molecula*, diminutive of *moles*—the mass), by further division they are resolved into dissimilar parts. Hence, iron sulphide is made up of molecules, which in turn consist of atoms of iron and of sulphur. We shall learn later that the elements—with few exceptions—are composed, at ordinary temperature, not of a collection of free atoms, but of an aggregation of atom-groups—of molecules. A molecular structure is the rule. In the case of the elements the molecules are composed of like kinds of atoms, in compounds they consist of dissimilar atoms.

The greatest advancement of the atomic theory is due to John Dalton. By assuming that the atoms combined with one another in definite proportions, he laid the basis for the determination of the *relative atomic weights*, and thereby became the founder of the chemical atomic theory based upon definite weight proportions (1804). If two elements form but a single compound by union with one another, it may be assumed with Dalton, as long as no other reason to the contrary exists, that their molecules consist of an atom of each of the two elements. Should two compounds of the elements A and B be known, then the molecule of the one compound would consist of an atom each of A and of B, consequently of two atoms, while the other compound might be composed of three atoms ($2\ A + B$ or $2\ B + A$), etc. With these premises clearly enunciated it is possible to determine the relative atomic weights of the elements.

One hundred parts of the previously mentioned iron sulphide consist in round numbers of 63.6 parts of iron and 36.4 parts of sulphur. If, however, in accordance with the assumptions of Dalton, there is in this compound one atom of sulphur for one atom of iron, then the atomic weights of iron and sulphur must be to one another as 63.6 : 36.4. The ratios between the atomic weights of the elements may be determined in this manner. If for any element a number be taken for its atomic weight, it can readily be calculated in what ratio the atomic weights of all the other elements stand to this arbitrarily chosen standard, and we thus obtain the *relative atomic weights*. That element which combines with the majority of the other elements to form compounds capable of the most accurate analysis, is chosen as the standard of comparison. Finally, the number or value assigned this standard element as its atomic weight is a matter of consensus of opinion.

Later we shall become acquainted with physico-chemical methods of testing the atomic numbers, derived in a chemical way, and especially for establishing whether it is not a fraction or a multiple of the true, relative atomic weight.

CHEMICAL SYMBOLS AND FORMULAS.

The chemical elements are simply and conveniently represented by the initials of their Latin or Greek names in accordance with the suggestion of the great Swedish chemist, John Jacob Berzelius (1779–1848) to whom we are also indebted for the first accurate atomic weight determinations. Thus hydrogen is designated by the letter H, from the word hydrogenium; nitrogen by N, from nitrogenium. Elements having the same initials are distinguished by adding a second letter; thus, Na indicates natrium (sodium), Ni—nickel, Hg—mercury (from hydrargyrum), Pd—palladium, Pt—platinum, etc.

The following table contains the names of 71 known chemical elements, together with their symbols and their atomic weights, *referred to oxygen equal to 16*.

It may be added :

That as a rule the atomic weights are given with only as many decimals as are accurate to the last figure. In the case of bismuth, nickel and tin, indicated by *, this rule is not adhered to. Also in the case of hydrogen the more accurate value 1.008 is given as 1.01 for ordinary use.

The elements whose names have ? attached are in doubt either as to their simplicity, or as to entire units in their atomic weights.

ELEMENTS.	SYMBOL.	ATOMIC WEIGHT.	ELEMENTS.	SYMBOL.	ATOMIC WEIGHT.
Aluminium, ...	Al	27.1	Neodymium (?), . . .	Nd	144
Antimony (Stibium), .	Sb	120	Nickel, ...	Ni	58.7*
Argon (?), ...	A	40	Niobium, ...	Nb	94
Arsenic, ...	As	75	Nitrogen, ...	N	14.04
Barium, ...	Ba	137.4	Osmium, ...	Os	191
Beryllium, ...	Be	9.1	**Oxygen**, ...	**O**	**16.00**
Bismuth, ...	Bi	208.5*	Palladium, ...	Pd	106
Boron, ...	B	11	Phosphorus, ...	P	31.0
Bromine, ...	Br	79.96	Platinum, ...	Pt	194.8
Cadmium, ...	Cd	112	Potassium (Kalium), .	K	39.15
Cæsium, ...	Cs	133	Praseodymium (?), . .	Pr	140
Calcium, ...	Ca	40	Rhodium, ...	Rh	103.0
Carbon, ...	C	12.00	Rubidium, ...	Rb	85.4
Cerium, ...	Ce	140	Ruthenium, ...	Ru	101.7
Chlorine, ...	Cl	35.45	Samarium (?), ...	Sm	150
Chromium, ...	Cr	52.1	Scandium, ...	Sc	44.1
Cobalt, ...	Co	59	Selenium, ...	Se	79.1
Copper, ...	Cu	63.6	Silicon, ...	Si	28.4
Erbium (?), ...	Er	166	Silver (Argentum), . .	Ag	107.93
Fluorine, ...	Fl	19	Sodium (Natrium), . .	Na	23.05
Gallium, ...	Ga	70	Strontium, ...	Sr	87.6
Germanium, ...	Ge	72	Sulphur, ...	S	32.06
Gold (Aurum), ...	Au	197.2	Tantalum, ...	Ta	183
Helium (?), ...	He	4	Tellurium, ...	Te	127
Hydrogen, ...	H	1.01	Thallium, ...	Tl	204.1
Indium, ...	In	114	Thorium, ...	Th	232
Iodine, ...	I	126.85	Tin (Stannum), ...	Sn	118.5*
Iridium, ...	Ir	193	Titanium, ...	Ti	48.1
Iron (Ferrum), ...	Fe	56.0	Tungsten (Wolfram), .	W	184
Lanthanum, ...	La	138	Uranium, ...	Ur	239.5
Lead (Plumbum), . . .	Pb	206.9	Vanadium, ...	Vd	51.2
Lithium, ...	Li	7.03	Ytterbium, ...	Yb	173
Magnesium, ...	Mg	24.36	Yttrium, ...	Y	89
Manganese, ...	Mn	55.0	Zinc, ...	Zn	65.4
Mercury, ...	Hg	200.3	Zirconium, ...	Zr	90.6
Molybdenum, ...	Mo	96.0			

In addition to the elements mentioned in the table the following are believed to have been observed in certain rare minerals: *terbium* (*mosandrium*, *philippium*, Zα, Zβ), *gadolinium*, *decipium*, *holmium*, *thulium* and *dysprosium*. They occur associated with cerium, lanthanum, scandium, ytterbium and yttrium. They are so much alike chemically that it is difficult to separate them and obtain them pure; they are probably mixtures of unknown elements.

Consult the paragraphs under Air for an account of what seem to be elementary gases (metargon, neon, krypton, xenon) which have been isolated from the atmosphere. For the reasons leading to the adoption of oxygen as the element of comparison and establishing its atomic weight as 16, see p. 73.

Compounds produced by the union of the elements are represented by placing their corresponding symbols together and designating these *chemical formulas*. Common salt, a compound of sodium and chlorine, is represented by the formula NaCl; mercuric oxide, a compound of mercury and oxygen, by HgO; iron sulphide by FeS; hypochlorous acid, a compound of hydrogen, chlorine and oxygen, by HClO.

By these premises chemical formulas acquire a very precise and evident importance. The formula NaCl represents the union of 1 atom of sodium with 1 atom of chlorine, and indicates that in it 23.05 parts, by weight, of sodium are combined with 35.45 parts by weight of chlorine to yield 58.50 parts of sodium chloride (common salt). If several atoms of an element are present in a compound, this is denoted by numbers which are attached to the symbol of the atom:

HCl	H_2O	NH_3	CH_4
Hydrochloric acid.	Water.	Ammonia.	Methane.

The formula of water (H_2O) means that its molecule consists of 2 atoms of hydrogen (2.02 parts by weight) and 1 atom of oxygen (16 parts by weight). The formula of sulphuric acid (H_2SO_4) indicates it to be a compound consisting of 1 atom of sulphur (32.06 parts), 4 atoms of oxygen ($4 \times 16 = 64$ parts), and 2 atoms of hydrogen ($2 \times 1.01 = 2.02$ parts), from which the composition of the acid may be at once calculated into per cent., or into any desired quantity by weight.

Atomic Composition.	In Per Cent.
Hydrogen, $H_2 = 2.02$	2.06
Sulphur, . . $S = 32.06$	32.69
Oxygen, . . $O_4 = 64.00$	65.25
$H_2SO_4 = 98.08$	100.00

A chemical change is represented by arranging these symbols in the form of an equation. The left side of the equation indicates the substances present before the reaction occurs, while the right side shows the products. Thus the *chemical equation*:

$$HgS + Fe = FeS + Hg$$

means that mercury sulphide (232.36 parts) and iron (56 parts) have combined to form iron sulphide (88.06 parts) and mercury (200.3 parts). The equation

$$2H + O = H_2O$$

indicates that 1 molecule of water has been formed by the union of 2 atoms of hydrogen with 1 atom of oxygen.

It is true these equations give no idea of the conditions surrounding these transpositions, nor of the alterations in energy which accompany them. They represent the purely material side of the change. They indicate the quantities by weight of the substances entering the reaction and also of the products: the weight of the bodies entering the reaction is equal to that of the resulting products. Every chemical equation is therefore an expression of the law of the indestructibility of matter (p. 20).

CONDITIONS OF CHEMICAL CHANGE.

THERMO-CHEMICAL PHENOMENA.

The first requisite for bodies to act chemically upon one another is that they be brought into most intimate contact because chemical action does not occur at great distances. In the case of solids this intimate contact, so essential for complete chemical transformation, cannot ordinarily be attained by mere mechanical mixing: the necessary condition is best reached by liquefying the bodies, or at least one of them, by fusion or solution in some solvent. Hence the old saying *corpora non agunt nisi fluida.*

In many instances, however, the chemical transposition does not take place even with the most intimate contact. An external physical impulse occasioned by light, by electricity, by change in pressure (Spring, van't Hoff), but more especially by the temperature, is required for its occurrence. Thus, for example, hydrogen and oxygen at the ordinary temperature are wholly indifferent to one another despite the fact that as gases they may be mixed as completely as it is possible. It is only when they are heated that they combine—slowly at 200°, but with violent explosion about 700°—to water. The same occurs upon passing the electric spark through the mixture. A mixture of hydrogen and chlorine will remain unchanged in the dark, while in diffused sunlight the gases will slowly unite to hydrochloric acid, but in direct sunlight, upon the application of heat, or by passing the electric spark they will unite at once with great violence. A mixture of iron and mercury sulphide requires the aid of heat to bring about the transposition to iron sulphide and mercury. At the ordinary temperature they appear to exercise no visible chemical action upon one another. By the application of external energy—heat, light, electricity, etc.—the atomic structure of the molecules of hydrogen and oxygen, of chlorine and hydrogen, of mercury sulphide and iron, etc.—is first loosened or disintegrated and then the chemical action between the several components takes place. However, the experiments of Raoul Pictet [1892; compare Ber. **26** (1893), IV, 1 and A. Welter, Die tiefen Temperaturen, Crefeld 1895] show that chemical reactions do not occur at temperatures below —125°. Substances which at the ordinary temperature react with the greatest readiness—*e. g.*, sulphuric acid and barium chloride, hydrochloric acid and silver nitrate, sodium and alcohol —appear at —80° to be as indifferent toward one another as mercury sulphide and iron, and hydrogen and oxygen at the ordinary temperature. Even such delicate tests as those of blue litmus and sulphuric acid or hydrochloric acid do not take place below —110°. It is obvious, therefore, that the power of substances to act chemically upon one another is entirely dependent upon the external conditions, particularly the temperature, prevailing at the moment of their contact. This has been further demonstrated by the experiments which it has been possible to conduct at very high temperatures. It is well known that hydrogen and oxygen unite to form water above 200°, but at 2000° and above, water breaks down again into hydrogen and oxygen (compare Dissociation of Water). The higher the temperature the more complete will be the decomposition, and eventually a point will be reached at which the hydrogen and oxygen will exert as little chemical action upon one another as they would below 200°.

A chemical compound is, therefore, only wholly stable within a certain range of temperature. The latter may change, however, with the pressure and in the case of some substances we may not be able to obtain it with our present facilities. The compound will begin to separate into its constituents—its elements—just as soon as this limit is exceeded. The rapidity of the decomposition, the magnitude to which it may extend, is also dependent upon pressure and temperature. This is therefore due to the fact that a portion of the product of decomposition reunites to form the original body and in this way a state of chemical equilibrium is produced. The extent of the decomposition is always definite for given external relations. Similarly, the action of unlike bodies upon one another is frequently complete only within definite ranges of temperature, and the rapidity with which this action proceeds is in like manner influenced not only by temperature but also by pressure and by quantity-relations. Very often opposite reactions, union and decomposition, occur simultaneously, and occasion a state of equilibrium.

Every chemical change is invariably accompanied by a change of energy—by the disengagement or absorption of heat (electricity, etc.). The customary chemical equations, such as are employed upon page 27, represent merely the material side of a chemical reaction, the nature and quantities by weight of the reacting and resulting substances. But when, for example, 2.02 grams of hydrogen and 16.00 grams of oxygen unite to yield water, there is an accompanying dynamical change, a definite and considerable quantity of heat is disengaged—in this instance equaling 68.4 calories (p. 23). An equation showing the union of hydrogen with oxygen to form water—an equation which would include both *weight* reactions and those of *energy*—would read as follows:

$$2H + O = H_2O + 68.4 \text{ Cal.}$$

Similarly, in the union of 1.01 grams of hydrogen with 35.45 grams of chlorine, forming 36.46 grams of hydrogen chloride, we have a liberation of 22 calories:

$$H + Cl = HCl + 22 \text{ Cal.};$$

while the formation of hydrogen iodide (127.86 grams) from hydrogen (1.01 grams) and iodine (126.85 grams) is accompanied by an absorption of energy—an absorption of 6 calories:

$$H + I + 6 \text{ Cal.} = HI.$$

But this equation is in no manner to be understood as meaning that hydrogen and iodine require the addition of but 6 calories in order that hydrogen iodide may result. The application of that amount of heat would only produce a warmed mixture of hydrogen and iodine vapor. The quantity of energy equivalent to 6 calories of heat can only be taken up by the mixture under certain definite physical conditions in such a way that hydrogen iodide is the product.

When we desire to decompose water into hydrogen or oxygen we must restore all the energy which has escaped. This energy is contained in the free elements as chemical (potential) energy. The decomposition of hydrogen iodide into its elements, on the contrary, occurs with a disengagement of heat. This heat is equivalent to the energy which the iodine and hydrogen took up in their passage into hydrogen iodide.

Reactions are distinguished as *exothermic* and *endothermic*, *i. e.*, they have *positive* or *negative thermal values* depending upon whether heat (energy) is liberated or absorbed.

The heat modulus, attending a chemical reaction, offers important conclusions as to the concurrent alterations in energy, as well as to the nature of the substances entering the reaction.

These relations are most evident in those reactions in which *only two elements* participate. Compounds, formed from their elements with the liberation of heat, contain less energy than the elements themselves, are more stable than their mixture, and can be resolved into the original elements by the consumption of energy. The conditions requisite for their formation are equally present in the mixture of the parent substances, because every system of bodies, as taught by mechanics, strives to attain that state of equilibrium, in which the content of energy, convertible into work, of tension or, as Helmholtz terms it, of *free energy*, is as low as possible. It is for this reason, therefore, that reactions of this description occur almost immediately on bringing the respective bodies together. An example of this kind has already been given: antimony and chlorine unite instantaneously to antimony chloride (p. 19). As a rule, however, an external impulse from heat, electricity, or light is needed to start the reaction. Several examples illustrating this have been presented. This behavior must be regarded as a sort of liberation of the chemical tension. It is necessary that a portion of the molecules—the physical individuals—first be resolved into their atoms—the chemical individuals—the combination of the atoms in the molecules must be made less intimate at least. When once the reaction has been in this manner begun at one point of the mixture, it generally continues and proceeds of itself, according to the amount of heat developed, with greater or less intensity, which may even reach to explosion, as in the production of water or hydrochloric acid from their elements.

Compounds which *absorb heat* when produced from their elements, *e. g.*, hydrogen iodide and nitrogen chloride, contain more free energy, more tension, than the parent substances, and are consequently less stable than their mixture. They cannot be formed from their elements without the simultaneous addition of energy. In this instance to simply initiate the reaction is not sufficient, for energy must be continually added, otherwise the chemical action will cease.

Viewed thermally, the decomposition of compounds into their elements proceeds oppositely to their formation. If the latter was accompanied by heat evolution then the decomposition would occur with heat (energy) absorption, would require the constant addition of energy, advance very gradually, never in an explosive manner, and would be circumscribed by the opposing combination-tendency of the products of the decomposition (compare Dissociation of Water). Just as every transition of a system from a condition of stability to one of less stability requires an expenditure of work, so does the decomposition of such a body as indicated in the preceding lines. Compounds, however, which like hydrogen iodide and nitrogen chloride are produced with heat absorption, generally break down with ease and completely into their elements. In this way the system passes into a more stable condition. Frequently, an external impulse is all that is necessary to start such a decomposition. It then proceeds of its own accord and may increase even to explosion. Many of the bodies belonging in this group are explosive; indeed, some of them, *e. g.*, chlorine monoxide and nitrogen iodide explode when touched or when warmed, others again require a more energetic concussion. Thus, nitric oxide, acetylene, and cyanogen explode if a slight amount of mercury fulminate be ignited in them.

The heat modulus is not a measure of the affinity of the elements which combine with one another. Even the formation of water from hydrogen and oxygen, an apparently very simple process, is really the product of a number of chemical and physical changes, proceeding by grades, which in turn are accompanied partly by positive and partly by negative thermal values—breaking down of the molecules into atoms, union of the different atoms to molecules; diminution of the number of molecules, liquefaction of the aqueous vapor. The quantity of heat observed merely represents the algebraic sum of all these heat moduli (thermal values).

If more than two elements, if several compound substances, take part in a chemical change the meaning of the thermal value accompanying it is more difficult to comprehend. The majority of reactions of this kind proceed in harmony with *the principle of greatest heat development* according to which from a given system of bodies, without the introduction of external energy, that new compound will result, in whose formation there is the greatest heat development (Berthelot). This principle is not universally acknowledged, neither do all the facts support it, nor is it justified from the standpoint of the mechanical theory of heat. The entropy-principle is a more acceptable substitute (p. 23). When the thermal relations of the various groups of elements and compounds are discussed this point will be more minutely considered.

28

THE PRINCIPLES OF CRYSTALLOGRAPHY.

to 37

25

Solid, homogeneous bodies are composed of the smallest particles, *molecules*, which we imagine as being irregularly placed or arranged in a regular net-like manner. In the first instance they are *amorphous*, showing like physical properties in every direction, while in the second case they are *crystallized*, manifesting a similar physical deportment in all parallel directions, but which in general varies in different directions.

In crystallized bodies the molecules are so arranged in layers, that all the particles are similar. These layers form planes, *crystal faces*, whose form depends on the nature of the molecules; in crystals differing from one another chemically, the form of the faces is also different.

A combination of all the crystal faces (planes) circumscribing a crystallized body constitutes its *crystal form*, which is always definite for every crystalline chemical compound. The form and the extension of the individual faces may vary, but the angles produced by the faces remain unchanged. (Law of the constancy of angles formed by crystal faces.)

A *zone* is produced by three or more planes cutting one another in parallel edges; the *zone axis* is the direction with which the edges run parallel.

We can imagine most crystals so divided by planes that each crystal face upon the one side corresponds to a similar face on the opposite side, producing a like angle with the intersecting plane. Such a plane is designated a *symmetry-plane;* its perpendicular is known as the *symmetry axis.*

The *symmetry ratios* vary with the individual crystals. One may exhibit greater symmetry—more symmetry-planes—than another. All those crystalline forms in which there is a like number of symmetry-planes constitute a system of crystallization.

There are two kinds of symmetry-planes. Thus crystals exhibit in part one or several symmetry-planes, with which several symmetry axes are parallel and which may be exchanged one for the other without altering the crystalline form. Symmetry axes of this description are said to be *equivalent*, and the symmetry-planes with which they are parallel are called the *principal symmetry-planes* and their perpendiculars are the *principal axes.*

Six systems of crystallization are distinguished on the basis of relations in symmetry.

I. The *regular* or *isometric system* with three principal symmetry-planes and six secondary symmetry-planes.

II. The *hexagonal system* with one principal symmetry-plane and six symmetry-planes.

III. The *quadratic* or *tetragonal system* with one principal symmetry-plane and four secondary symmetry-planes.

IV. The *rhombic system* with three secondary symmetry-planes.

V. The *monoclinic system* with one secondary symmetry-plane.

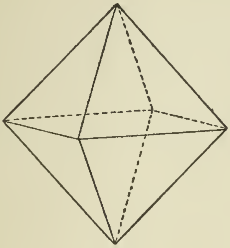
VI. The *triclinic system*, in which there is no symmetry-plane.

I. The Isometric System.—The forms of this system are referred to an axis system consisting of three axes of equal length (*principal symmetry axes*) and at right angles to one another. Two of the axes lie in a principal symmetry-plane. The various fundamental forms are derived by imagining these axes a, a, a, cut by planes at equal or unequal distances from their point of intersection. The axial section of a plane is termed its parameter. If the smallest of these be designated by a, and the other two by na and ma, then the values n and m (the coefficients of the parameters) become in accordance with experience *rational* numbers. There are seven fundamental forms:

1. *Octahedron* (O) (Fig. 1). The faces intersect the axes at equal distances $a : a : a$ from the center.

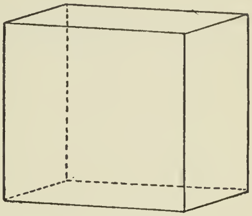
2. *Cube* ($\infty O \infty$) (Fig. 2). The faces intersect one axis and are parallel to the other two: $a : \infty a : \infty a$.

3. *Dodecahedron* (∞O) (Fig. 3). The faces intersect two axes at the same distance from the center, while they are parallel to the third axis: $a : a : \infty a$.



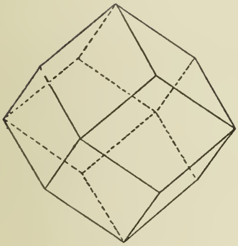
O

FIG. 1.



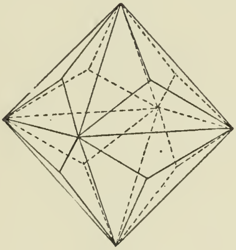
$\infty O \infty$

FIG. 2.



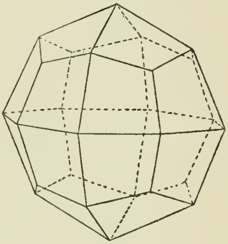
∞O

FIG. 3.



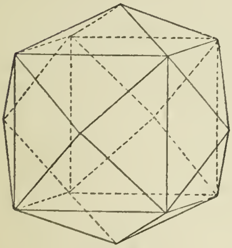
$2O$

FIG. 4.



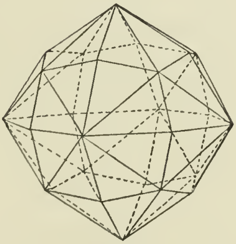
$2O2$

FIG. 5.



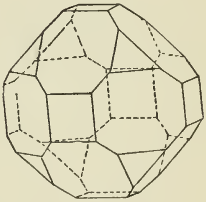
$\infty O2$

FIG. 6.



$3O\frac{3}{2}$

FIG. 7.



$\infty O, \infty O \infty . O$

FIG. 8.

4. *Trisoctahedron* (mO) (Fig. 4). The faces intersect two of the axes at unity and the third at a greater distance: $a : a : ma$.

5. *Trapezohedron* or *Icositetrahedron* (mOm) (Fig. 5). The faces intersect one axis at unit distance and the other two at equal but greater distances: $a : ma : ma$.

6. *Tetrahexahedron* ($\infty O n$) (Fig. 6). The faces intersect two axes at different distances and the third axis at infinity: $a : na : \infty a$.

7. *Hexoctahedron* ($m O n$) (Fig. 7). The faces cut all three axes at different distances: $a : na : ma$.

These *simple* forms usually occur in *combination;* this is also true of the remaining systems. Thus Fig. 8 represents the combination of dodecahedron (∞O), cube ($\infty O \infty$), and octahedron (O).

II. The Hexagonal System.—There are seven symmetry-planes in this system, six of which are at right angles to the seventh—the principal symmetry plane. The six planes referred to cut one another at an angle of 30°. The intersecting lines of three alternating planes (cutting one another at 60°), together with the principal symmetry-plane, are regarded as the secondary axes (these are equal $a : a : a$). The fourth axis is the axis (c) at right angles to the principal symmetry-plane. The ratio $a : c$ is irrational and is very definite for every substance crystallizing in the hexagonal system.

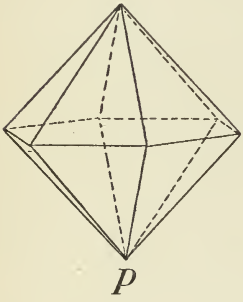


FIG. 9.

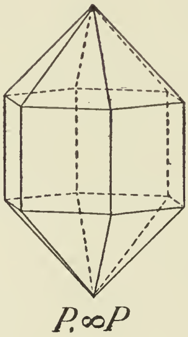


FIG. 10.

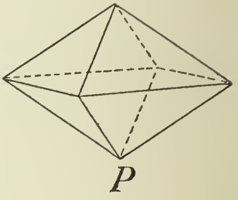


FIG. 11.

The forms of this system are either *double pyramids* consisting of twelve or six faces converging above and below at the terminals of the principal axis, or they are twelve- or six-sided *prisms*, the faces of which are parallel to the principal axis. To these must be added the pair of faces perpendicular to the principal axis—the *basal planes.* Fig. 9 represents the *hexagonal pyramid* (P) and Fig. 10 the *hexagonal pyramid* (P) with the *prism* (∞P). The angle produced by the intersection of two prism faces equals 60°.

III. Tetragonal or Quadratic System.—This system like the hexagonal is characterized by a single principal symmetry-plane to which four alternating similar symmetry-planes cutting one another at 45° are perpendicular. There are three axes at right angles to one another. The principal axis (c) is normal to the principal symmetry-plane, while the other two (a, a) correspond to the intersecting directions made by two equal symmetry-planes with the principal symmetry-plane.

The forms of this system, as in the hexagonal system, consist of pyramids, prisms, and basal plane (pinacoid). The pyramids are made up of four or eight faces above and below. The prisms also have four or eight faces; *e. g.*, Fig. 11: *tetragonal pyramid* (P); Fig. 12: *tetragonal* prism (∞P) with the *pyramid* (P). The angle formed by two prism faces is 90°.

IV. The Rhombic System.—In this system there are three dissimilar symmetry-planes at right angles to one another. Their directions of intersection are assumed to be the axes a, b, c. The *rhombic pyramid* (P) (Fig. 13) is the fundamental form. It cuts the three axes (of unequal lengths) at their unit distances (a is the *brachy-axis*, b the *macro-axis*, and c the *vertical axis*). There are other pyramids in which the faces intersect the axes at other than unit distances from the center. Prismatic forms result when the faces are parallel to one axis. If they are parallel to c the *rhombic prism* (∞P) (Fig. 14), and *macro-* or *brachydomes* if the faces run parallel to b or a, *e. g.*, Fig. 15, the *macrodome*.

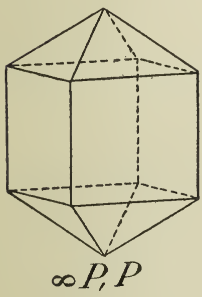


FIG. 12.

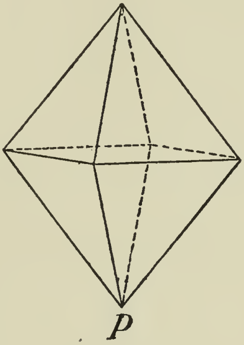


FIG. 13.

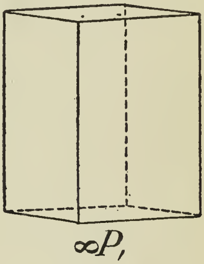


FIG. 14.

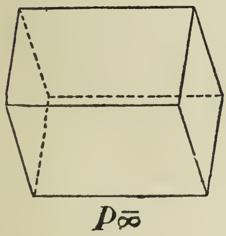


FIG. 15.

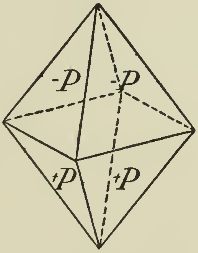


FIG. 16.

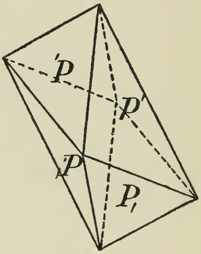


FIG. 17.

The pair of faces perpendicular to the vertical axis constitutes the *basal planes*, while the other pairs of faces at right angles to the other two axes are termed the *macro-* and *brachy-pinacoids*.

V. The Monoclinic System.—There is but one symmetry-plane in this system. It is directed toward the observer when he examines the crystals. The axis system consists not only of the perpendicular (b-axis) to the symmetry-plane, but also of the intersecting lines (a and c), which form two crystal faces with and at right angles to the symmetry-plane and are inclined to one another at any arbitrary angle (β). The vertical axis is c, while a, directed toward the observer, is designated the *clino-axis.* The forms are like those of the rhombic system. Each pyramid, however, resolves itself into two independent *hemi-pyramids;* these are distinguished as positive ($+ P$) and negative ($— P$) (Fig. 16). There are positive and negative orthodomes, each arising from a pair of faces, which correspond to the rhombic macrodomes. The prismatic form, parallel to the clino-axis, is termed the *clinodome.*

VI. Triclinic System.—Any three crystal planes are selected for the axis-planes. Their intersecting lines constitute the axes a (brachydiagonal), b (macrodiagonal), c (vertical axis). All the axes intersect one another at oblique angles. The angle between b and c is designated α, that between a and c β, and that between a and b γ. There is no symmetry-plane present; each parallel pair of faces constitutes a crystal form, so that a pyramid intersecting the three axes at the distances $a : b : c$ consists of four different crystal forms which are marked as in Fig. 17 with P', $P_{,}$, $'P$, $_{,}P$. All the other forms, as in the monoclinic system, are derived from these, with the difference that in this system the distinction between right and left must be observed.

In nature, crystals rarely occur so regularly developed as represented in the preceding forms. Usually they are more or less elongated in one or more directions and this causes the faces of one and the same form to become, as regards their spacial extension, unequal and the whole crystal appears to be distorted. Such a distortion, however, never influences the position of the faces with reference to the axes. The angles produced by the faces remain unchanged so long as the temperature is the same. (Law of the constancy of the angles formed by the faces.) The measurement of the angle formed by the faces by means of the goniometer is the only means we possess of unraveling complicated combinations, and even this aid is not in all cases satisfactory in determining definitely and surely that a form belongs to one or another system. For this purpose a careful investigation of the physical properties is frequently essential, because it occurs that crystals apparently develop a higher symmetry geometrically than belongs to them when their physical properties are considered (pseudo-symmetric crystals).

Another irregularity in their development consists in the fact that the faces themselves are not even and smooth. They frequently occur bent, *e. g.*, in the diamond and dolomite; drusy, due to the protuberance of numerous little solid angles, upon the faces, of other forms differently orientated, or striated by the frequent alternating appearance of two faces—*e. g.*, the striation of the cube faces of pyrite due to the oscillatory appearance of a pentagonal dodecahedron—rough, corroded, etc., etc.

Two or more crystals are often grown together; this growth being either regular or irregular. When regular the crystals are parallel to one another and are designated *parallel growths*, or they are not parallel but yet limited by a very definite regularity. Such growths are called *twins.*

Their regularity consists in the fact that the two crystals forming the twin are symmetrically developed with one another in relation to a crystallographically possible plane—the *twinning-plane.* Fig. 18 represents an example of such a twin crystal. Two octahedra, or better, two half octahedra, are here symmetrical in reference to an octahedral face. Spinel and magnetite are examples of this class. The plane along which the two individuals have developed is the growth-plane. It is not necessary that this should at the same time be the twinning-plane, for two crystals can be symmetrical to one another in reference to one plane and yet be developed along another plane. This, for example, is often the case with what are termed the Carlsbad orthoclase twins. In them the clino pinacoid is the growth-plane and the orthopinacoid the twinning-plane.

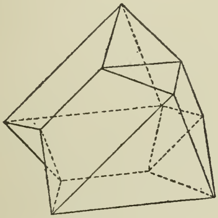


FIG. 18.

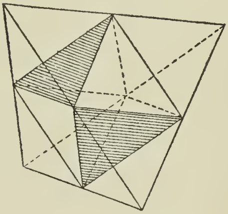


FIG. 19.

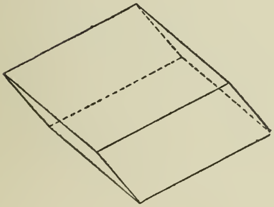


FIG. 20.

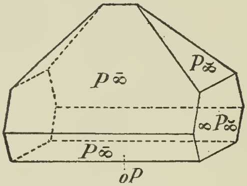


FIG. 21.

Crystals may also grow on both sides beyond the growth-plane, *penetration-twins* or crosses are the result.

In addition to the simple forms appearing with all their faces, hence termed *holohedral form*, others occur in which only half the possible faces are present—the *hemihedral form.* These result if we imagine a holohedral form to be divided by symmetry-planes into congruent parts, and then have one of every two parts, which are symmetrical in reference to these planes, fall away. In this manner every holohedral figure will yield *two* hemihedral forms which differ from one another in their position, and are either congruent or symmetrical. Thus, the octahedron of the isomeric system yields the *tetrahedron*, Fig. 19, and the hexagonal pyramid, the *rhombohedron* (Fig. 20).

A comparatively rare phenomenon has been observed in the crystals of some substances—namely, a different development at the opposite ends of an axis. This is known as *hemimorphism*. Struvite (magnesium ammonium phosphate $Mg(NH_4)PO_4 + 6\ H_2O$), Fig. 21, is an example of this. On the upper end of the vertical axis occur the domes $P\ \bar{\infty}$ and $P\ \breve{\infty}$, while below there is only the dome $P\overline{\infty}$ and the basal plane oP. Tourmaline, calamine, cane sugar, etc., exhibit the same phenomenon.

Substances crystallizing variously in the same, or in two or three different systems are said to be *dimorphous*, *trimorphous*, etc. Titanium dioxide (TiO_2), for example, is found in nature in crystals of the quadratic system as the minerals anastase and rutile, and in those of the rhombic system as brookite (see also Sulphur).

Various substances which crystallize in similar or in forms very much alike in the same system are called *isomorphous* (see also Isomorphism).

SPECIAL PART.

CLASSIFICATION OF THE ELEMENTS.

Ordinarily we are accustomed to divide the elements into two groups: metals and non-metals (see p. 19). The former possess metallic appearance, are good conductors of heat and electricity; the latter, the metalloids or non-metals, do not have these properties, or at least in less degree. In chemical respects the metalloids have the tendency to combine with hydrogen, forming volatile, generally gaseous, compounds; their oxygen derivatives form *acids* with water. The metals, on the contrary, do not unite with hydrogen, or at least do not form volatile compounds with it, and their oxygen derivatives yield chiefly the so-called *bases* with water. Further, the compounds of metals with the non-metals are so decomposed by the electric current that the metal separates at the electro-negative, and the non-metal at the electro-positive pole. From this we observe the metals are more electro-positive—more basic; the metalloids more electro-negative—of an acid-forming nature. A sharp line of difference between metals and metalloids does not exist. There are elements, like antimony, which in their external appearance resemble metals, while in a chemical respect they deport themselves throughout as metalloids, and vice versâ. Thus hydrogen, a gaseous element, is like the metals in its entire chemical character, while metallic antimony arranges itself with the metalloids.

It is therefore better to divide the elements into separate natural groups, based upon their chemical analogies. The best and only correct classification of all the elements depends on the law of *periodicity*, according to which the properties of the elements and of their compounds present themselves as a *periodic function* of the *atomic weights*. Later we shall treat of the periodic system more at length; it forms the basis of this text-book, and in accordance with this doctrine we consider the elements in single natural groups of similar chemical deportment. The first of these groups, comprising almost all the so-called non-metals, are the following:

Fluorine	Oxygen	Nitrogen	Carbon	Boron
Chlorine	Sulphur	Phosphorus	Silicon	
Bromine	Selenium	Arsenic		
Iodine	Tellurium	Antimony		

Hydrogen does not belong to any of these groups; uniting the metallic and non-metallic characters in itself, it represents, as it were, the type of all elements, and therefore it will receive first attention. Boron occupies an isolated position. It has been classed with the non-metals, but differs somewhat from them in chemical deportment. It forms the transition to the metallic elements, beryllium and aluminium.

HYDROGEN.

Atom: $H = 1.01$. Molecule: $H_2 = 2.02$.

Hydrogen (hydrogenium), a gaseous body, occurs rarely in a free condition upon the earth's surface,—in the gases from volcanoes and in those issuing from the earth,—as an enclosure in minerals, a product of decay, and, from recent statements, it is found in very small amount in the atmosphere. It is, however, present in considerable quantity in the photosphere of the sun and fixed stars. In combination, it is found chiefly as water, and in substances of vegetable and animal origin. Paracelsus first observed this element in the sixteenth century, and called it inflammable air; and in 1766 Cavendish, recognizing it as a peculiar gas, named it inflammable air. In 1783 Lavoisier proved that hydrogen was a constituent of water—a chemical compound of the elements hydrogen and oxygen—by conducting steam over ignited metallic iron.

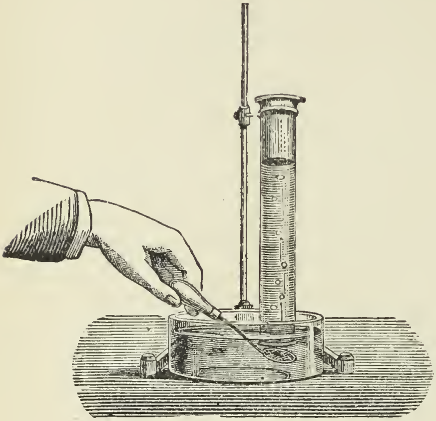


FIG. 22.

Preparation.—It may be readily obtained from water. The decomposition of the same by the removal of oxygen can be effected by some metals, like sodium and potassium, at the ordinary temperature. Both metals act very energetically upon it, liberating gaseous hydrogen. To perform the experiment, take a piece of sodium, roll it up in a piece of wire gauze, and shove it, with nippers, under the mouth of a glass cylinder filled with and inverted over water (Fig. 22). Bubbles of hydrogen are at once disengaged, displace the water and collect in the upper part of the cylinder. The reaction occurring between the sodium and water is expressed by the following chemical equation:

$$\underset{\text{Water.}}{H_2O} + \underset{\text{Sodium.}}{Na} = NaOH + \underset{\text{Hydrogen.}}{H.}$$

The compound NaOH, known as sodium hydroxide, remains dissolved in the excess of water.

Other metals decompose water in a similar manner, at an elevated temperature. To effect this with iron allow steam to pass through a tube filled with iron filings, exposed to a red heat in a combustion furnace. The iron withdraws oxygen from the water, combining with it, while the hydrogen set free is collected. Magnesium powder reacts similarly, but at a much lower temperature, upon steam (Ber. 26 (1893), I, 59).

For laboratory purposes, hydrogen is prepared by the action of zinc upon hydrochloric or sulphuric acid. The reaction with the latter acid is as follows:

$$\underset{}{Zn} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + H_2.$$

Place granulated zinc (obtained by dropping molten zinc into water) in a double-necked flask (Fig. 23), and introduce sulphuric acid (diluted with about 3 vols. of H_2O) through the funnel tube, b. The liberation of gas begins immediately, and the hydrogen, escaping through the exit tube, f, is collected as previously described.

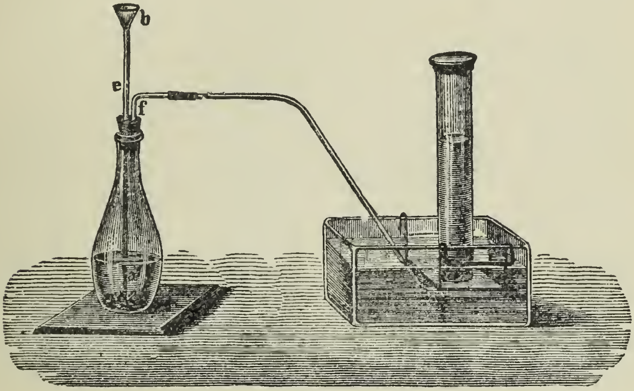


FIG. 23.

The hydrogen thus formed has a faint odor due to a slight admixture of foreign substances (the hydrides of sulphur, arsenic, phosphorus and carbon—if these elements are contained in the metal used in the gas evolution). It is therefore conducted through a solution of potassium permanganate to purify it.

Many other metals, *e. g.*, iron, behave like zinc with dilute acids. Some metals—zinc, iron, and aluminium—dissolve, when finely divided, in sodium or potassium hydroxide with the liberation of hydrogen:

$$Zn + 2NaOH = Zn(ONa)_2 + H_2.$$

Pure hydrogen may be obtained by heating potassium formate with potassium hydroxide: $CHO_2K + KOH = K_2CO_3 + H_2$; for technical purposes by heating zinc or iron with calcium hydroxide (slaked lime) in a combustion tube: $Zn + CaO_2H_2 = ZnO + CaO + H_2$, or with coal (anthracite):

$$2CaO_2H_2 + C = CaCO_3 + CaO + 2H_2.$$

A very important method for the preparation of hydrogen consists in decomposing certain aqueous solutions by means of the electric current. This decomposition usually proceeds as if the water broke down into its constituents: $2H_2O = 2H_2 + O_2$. The hydrogen appears at the negative pole. The electrolysis of such solutions will be discussed exhaustively later.

Purifying and Drying of Gases.—To free gases of the substances mechanically carried along during their disengagement, it is best to conduct them through variously constructed wash-bottles, filled with water or liquids, which will absorb the impurities. Ordinarily the so-called Woulff bottles are employed (compare Figs. 31 and 35). The open tube, placed in the middle tubulure, is called the safety tube. It serves to equalize the inner pressure with that of the external atmosphere. Wash-bottles of various construction will be represented in the several sketches.

Gases liberated from an aqueous liquid are always moist, as they contain aqueous vapor. To remove this conduct them through vessels or tubes filled with hygroscopic substances (see Fig. 30). Calcium chloride, burnt lime, sulphuric acid, etc., are used for this purpose.

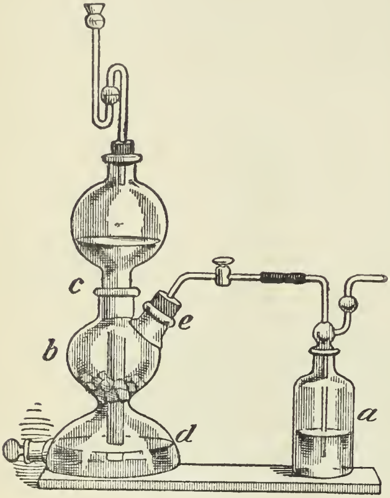


FIG. 24.

Apparatus for the Generation and Collection of Gases.—In the apparatus pictured in Fig. 23, the liberation of hydrogen continues uninterruptedly as long as zinc and sulphuric acid are present. To control the generation of the gas we have recourse to different forms of apparatus. One of the most practicable of these is that of Kipp. It consists of two glass spheres, *d* and *b*, Fig. 24, in the upper opening of which there is a third sphere, *c*, fitting air-tight and provided with an elongated tube. It serves as a funnel. Granulated zinc is placed in the middle sphere through the tubulure *e*, and dilute sulphuric acid is poured into the spherical funnel, which first fills *d*, then ascends to *b*, where it comes in contact with the zinc; at once the evolution of hydrogen commences and the gas escapes through *e*. Upon closing the stop-cock of the tube fixed in *e*, the hydrogen which is set free presses the sulphuric acid out of *b*, and consequently the liberation of the gas ceases. On again opening the stop-cock, the acid rises in *b* to the zinc, and the evolution of gas commences anew. The vessel *a* contains water or concentrated sulphuric acid to wash the escaping hydrogen.

The somewhat complicated Kipp apparatus may be advantageously replaced by the following simple contrivance recommended by Debray (Fig. 25). Two bottles provided with openings near their bottom, in which are glass tubes, are connected by a rubber tube. The bottle *A* is filled with granulated zinc, and *B* with dilute sulphuric acid. The cock *R* closes *A*. When this is opened the sulphuric acid flows from *B* to *A*, to the zinc, and the evolution of gas commences. *D* represents a form of wash-bottle suggested by Kempf. The gas evolution can be quickly regulated by raising or lowering the bottle *B*.

The Mohr apparatus (Fig. 26) is very convenient for the evolution of gases. Into the second cylinder containing the acid another narrower cylinder closed by a stop-cock is introduced. The zinc (iron, marble, etc.) is placed above the contraction of the inner cylinder. On opening the stop-cock the acid enters and evolution of gas commences. On closing the stop cock the hydrogen presses the acid back from the inner cylinder; the evolution of gas ceases.

Gasometers of various construction serve to collect and preserve gases. In Fig. 27 we have the ordinary gasometer of Pepys. It is constructed of sheet copper or zinc, and consists of two cylindrical vessels, the lower one closed, the upper open, communicating with each other by the two tubes *a* and *b*. The tube *c* is only a support. To this end, pour water into the upper cylinder, and open *a* and *e*; the water then flows through *a*, nearly reaching the bottom of the lower cylinder, while the air escapes through *e*. When the lower cylinder is filled with water close *a* and *e* (the last traces of air can be removed by opening *b*). To fill the gasometer with gas, remove the cover of the side tubulure *d*, and introduce the tube from which the gas is escaping. The latter rushes up into the cylinder, while the water flows out the tubulure. When the water is displaced by the gas, close *d*, after filling the upper cylinder, and then, if desired, open *a*, and the gas can be set free, either by *e* or *b*.

In addition to the gasometer described, various other forms are employed; gas-bags and tubes are very well adapted for preserving gases.

Physical Properties.—Hydrogen is a colorless, odorless, and tasteless gas. It conducts heat and electricity better than all other gases. This may be readily proved by the following experiment: A current of electricity is sent through a thin platinum spiral, and while the latter remains in the air or some other gas, it will glow, but in an atmosphere of hydrogen the spiral will not become luminous, or at once cease glowing. The metallic nature of hydrogen is shown by this behavior.

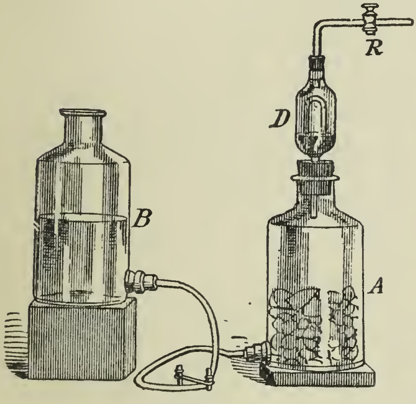


FIG. 25.

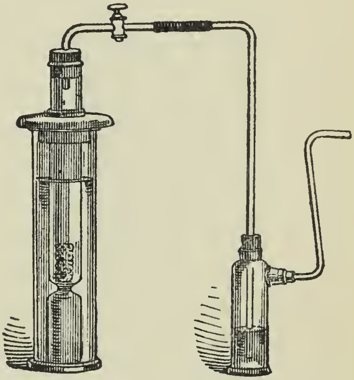


FIG. 26.

Of all gases hydrogen is the most difficult to liquefy, because its critical temperature is the lowest (about —220°); it must, therefore, be exposed to the most intense cold.

The procedure first adopted by Olszewski and more recently by Dewar for the production of liquid hydrogen (also applied to other gases) consists in suddenly lowering the pressure of the sufficiently cooled and powerfully compressed gas, when it will rapidly expand and a portion of it will deprive another portion of so much heat that the second portion will liquefy. Dewar permitted hydrogen cooled to —205° and under a pressure of 180 atmospheres to enter a vacuum-vessel also cooled to —200°.

The liquid hydrogen prepared in this way is colorless, very mobile and has the specific gravity of 0.07. It boils at about —240° under the ordinary atmospheric pressure.

Like all gases, coercible with difficulty, hydrogen is but slightly soluble in water, 1000 volumes dissolving 19 volumes of the gas at 14° C. The coefficient of absorption of hydrogen by water is therefore 0.0193. It is the lightest of all gases. That is, a definite volume of it weighs less than an equal volume of any other gas at the same temperature, under like pressure, and subject to a like action of gravity. It is generally understood that the comparison of the weight of equal gas volumes is made at 0°, 760 mm. barometric pressure at sea-level and in the 45° of geographical latitude. These are normal conditions, and under them 1 liter of hydrogen weighs 0.08988 gram, 1 liter of oxygen: 1.4291 grams, and 1 liter of air: 1.2930 grams. The thousandth part of each number, the weight of one cubic centimeter, is the specific gravity of the gas referred to water at 4°.*

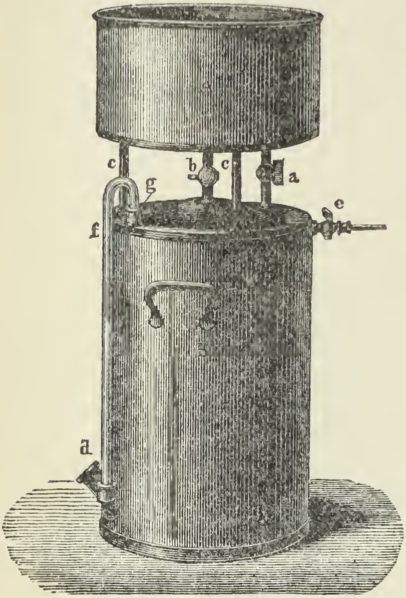


FIG. 27.

FIG. 28.

From this it follows that air is 14.4 ($= \frac{1{\cdot}293}{0{\cdot}08988}$) times heavier than hydrogen, and oxygen 15.9 ($= \frac{1{\cdot}4291}{0{\cdot}08988}$) times heavier than the latter. These numbers are the densities of these gases referred to hydrogen as unit. If, however, the weight of the air volume is selected as unit we obtain 0.06951 ($= \frac{0{\cdot}08988}{1{\cdot}293}$) as the density of hydrogen, and 1.1052 ($= \frac{1{\cdot}4291}{1{\cdot}293}$) as that of oxygen. It has become the rule quite recently in chemical discussions to refer densities to that element which is taken as the standard in atomic weights: oxygen, and for reasons which will be given subse-

---

* For the determination of these numbers compare Morley, Z. phys. Ch. 17 (1895) 87; 20 (1896) 68, 242, 417, and Thomsen, Z. f. anorg. Ch. 12 (1896) 1; also Kohlrausch, Leitfaden der prakt. Physik, 8 Aufl. (1896), 459. Morley gives as the most probable values for the weight of a liter of hydrogen and that of oxygen: 0.089873 and 1.4290; Thomsen: 0.089947 and 1.42906.

quently, the weight of its volume is placed at 32. Then for hydrogen there would result the number 2.0126 and for air 28.954.

The volume expressed in cubic centimeters which 1 gram of gas would occupy under normal conditions is its *specific volume*. If the weight of one cubic centimeter of gas is represented by a, its specific volume would be $V_s = \frac{1}{a}$. Hence the specific volume of hydrogen is $\frac{1}{0.08988} = 11,126$; that is, one gram of hydrogen under normal conditions occupies 11,126 cubic centimeters (11.12 liters). The specific volume of air is $\frac{1}{0.001293} = 773.4$ c.c., and that of oxygen $\frac{1}{0.0014291} = 699.7$ c.c.

That hydrogen is lighter than air is shown by a balloon of collodion or gum filled with the former rising in the latter; this can also be seen in soap bubbles filled with hydrogen. In consequence of its levity, hydrogen may be collected in inverted vessels (opening turned down) by displacing the air, and can also be poured from one cylinder into another, as represented in Fig. 28. The hydrogen flows from the inclined cylinder into the one held vertically and filled with air, which it expels. Such a separation of gases, based on their varying specific gravity, is only temporary, as they soon mingle with each other by diffusion. By virtue of its levity and mobility, which the kinetic gas theory attributes to the great velocity of the gas particles, hydrogen penetrates porous bodies with ease, and diffuses through both animal and vegetable membranes, as well as through gutta-percha (consult Air, upon diffusion of gases). Metals, *e. g.*, iron, platinum, palladium, permit a free passage to hydrogen, when they are raised to a red heat. They are impenetrable to other gases (see Dissociation of Water). This behavior is in part probably dependent upon the chemical attraction of these metals for hydrogen.

Chemical Properties.—Hydrogen is characterized by its ability to burn in the air, when it combines with the oxygen of the latter and forms water; hence its name hydrogenium, due to Lavoisier (from ὕδωρ, water, and γεννάω, I produce). Its flame is faint blue, and almost non-luminous, but possesses a very high temperature. When a mixture of hydrogen and air is ignited a violent explosion ensues; therefore, before bringing a light in the vicinity of hydrogen disengaged in a vessel filled with air, allow the latter to escape completely, otherwise the vessel will be shattered to pieces by the explosion.

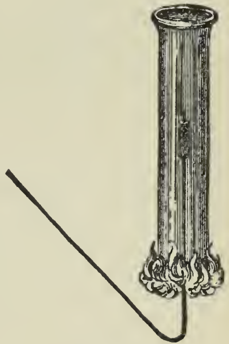


FIG. 29.

As hydrogen itself is inflammable, it cannot sustain the combustion of other bodies which will burn in the air. If a burning candle be introduced into an inverted cylinder containing the gas (Fig. 29) the latter will ignite at the mouth of the vessel, but the candle will be extinguished.

Water is the product of the combustion of hydrogen in the air. It is a chemical compound containing hydrogen and oxygen. To render the formation of it visible, by the combustion of hydrogen, the flame of the latter is made to burn under a cold glass jar (Fig. 30). The sides of the latter are soon covered with moisture, which collects in drops. To avoid any deception the hydrogen is first conducted through sulphuric acid or a tube filled with calcium chloride, to absorb all moisture.

At the ordinary temperature hydrogen and oxygen do not react without the intervention of a third substance.

The union of hydrogen with oxygen to form water occurs at about 200° (compare p. 28), if brought in contact with a flame, or by the passage of an electric spark through the mixture. The combination can be effected at ordinary temperatures with the aid of platinum sponge or palladium (platinum sponge, palladium asbestos); the platinum sponge consists of finely divided metal, obtained by the ignition of ammonio-platinum chloride (see Platinum). If a stream of hydrogen be directed upon a piece of freshly ignited platinum sponge, the gas will at once ignite. This is due to the power of the platinum to condense hydrogen and oxygen upon its surface, and thereby increase their ability to unite (*Dœbereiner lamp*).

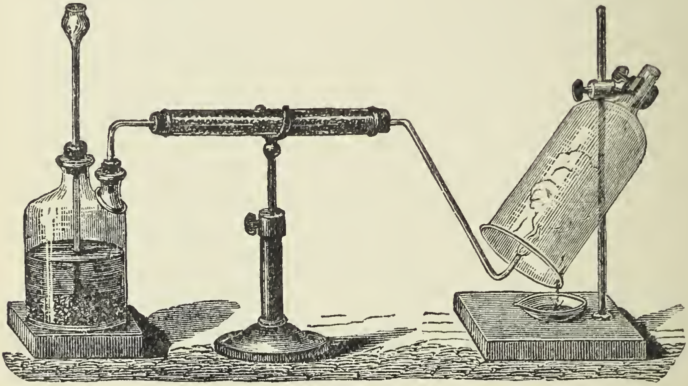


FIG. 30.

The absorption of hydrogen by the metal palladium is very characteristic. As already known, water is so decomposed by the electric current that hydrogen separates at the electro-negative pole and oxygen at the electro-positive. Now, if a piece of palladium, in sheet or wire form, be attached to the electro-negative pole, the disengagement of hydrogen does not occur, because it is absorbed by the palladium, in a quantity about eight hundred and fifty times the volume of the latter. Palladium also absorbs hydrogen when it is heated to 200°. The palladium expands, becomes lighter in weight, but retains its metallic appearance. Its tenacity and power of conducting heat and electricity are but little impaired. The compound of palladium and hydrogen, therefore, conducts itself like an alloy of two metals. From the specific gravity of the compound (according to Graham), the specific gravity of the condensed hydrogen is found to be 0.62 (water = 1), and is, therefore, somewhat heavier than the metal lithium (compare Palladium). The metals potassium and sodium absorb hydrogen when heated from 200° to 400°, forming alloys (Na_4H_2 and K_4H_2) in which the density of hydrogen is again equal to 0.62. The experiments of Winkler and of Moissan indicate that other metals also unite with hydrogen: barium, calcium, strontium, yttrium, lanthanum, cerium, and thorium. These facts prove the metallic character of hydrogen, which is also indicated by its ability to conduct heat and electricity. Later, we will observe that this element displays the character of a metal in its entire chemical deportment, and that it must be regarded as a gaseous metal at ordinary temperatures.

CONDENSATION OF GASES.

CRITICAL CONDITION.

Hydrogen and several other gases (oxygen, nitrogen, carbon monoxide, methane, nitric oxide), were considered until 1877 as non-condensable—permanent gases, inasmuch as all attempts to liquefy the same were failures, notwithstanding Natterer (1852) had employed a pressure of 3,600 atmospheres for this purpose. These negative results find their explanation in a general property of gases, first recognized by Andrews (1869), and called by him the *critical condition* of matter. There is a temperature common to all gases, above which they cannot be condensed—this is the *critical temperature.* It was first observed with carbon dioxide (see this). It can be liquefied at 0° under a pressure of 35.4 atmospheres, at 13° under 48.9 atmospheres, and at 30° under 73 atmospheres. Again, Cagniard de la Tour (1821) showed that all liquids when heated above a certain temperature (the same critical temperature), would be transformed into gases (absolute boiling point of Mendelejeff), although they were subjected to intense pressure (in sealed tubes). The pressure exerted by the gas at the critical temperature (at which it would immediately condense upon lowering the temperature) is called the *critical pressure;* the volume occupied by the substance at this time is the *critical volume.*

An additional interesting fact is the behavior of a liquid when it is gradually heated under a pressure which exceeds its critical pressure. When this is done the temperature can be increased to any extent without producing a noticeable separation into liquid and gas. At the critical temperature the liquid changes to gas without becoming heterogeneous and without sudden increase in volume. At the critical temperature and pressure the volume of the gas (or saturated vapor) is equal to the volume of an equal quantity, by weight, of the liquid. A difference between the gaseous and liquid condition no longer exists.

The critical condition also furnishes us with a criterion for the distinction between a gas, in the strictest sense of the word, and a vapor. A vapor by increase of pressure with constant temperature may become a liquid (or solid), while this is not possible with a gas. A gaseous body is, according to this idea, a permanent gas above the critical temperature, while below the same it is a condensable vapor.

To liquefy gases, we need not only pressure, but also a definite temperature, and this must be lower than the *critical.* By this means Cailletet and Pictet (1877) succeeded in condensing nearly all the permanent gases. Pictet pursued the method of Faraday, who had condensed various gases in sealed tubes (see Condensation of Chlorine, p. 51). The gases were generated in a powerful iron retort (oxygen from potassium chlorate; hydrogen from sodium formate) by the application of heat. They were then compressed under their own pressure in a copper tube attached to the retort. Solid carbon dioxide surrounded the tube, and by its evaporation under the air pump its temperature was reduced to —140°. On opening the stop-cock of the copper tube, the liquefied gas escaped in a stream which rapidly evaporated. Cailletet employed a capillary glass tube, provided with a reservoir and a pressure pump. The strongly compressed gas was cooled by opening a stop-cock and permitting it to expand suddenly. In its expansion and in overcoming the external pressure it performs work and there follows an absorption of an appreciable quantity of heat, which is taken from the gas. This causes a partial liquefaction of the gas in the form of a dense cloud, or in small drops.

With these facts as a basis Wroblewsky, Olszewsky, and more especially Dewar, Linde, and Ramsay have succeeded in condensing and retaining all gases in liquid form; indeed most of them have been solidified. Usually Cailletet's method has been pursued, care be taken to thoroughly cool the gas before the sudden decrease in pressure occurs (see Hydrogen and Air). Pictet's suggestion to strongly chill a greatly condensed gas has proved satisfactory for the condensation of several permanent gases to liquid form. Carbon dioxide, liquid ethylene, liquid oxygen, and nitrogen, which vaporize at slight pressure, have also been employed to produce the reduction in temperature. With a pressure of 10 mm. the temperature of liquid ethylene is reduced to —150°, liquid oxygen at 9 mm. to —211°, and liquid nitrogen to —225°. Lower temperatures than these, about —250°, are only attainable by the evaporation of liquid hydrogen.

Liquefied gases can be preserved quite well in Dewar bulbs: open, double-walled glass vessels, the intermediate space of which is a vacuum and the inner wall coated on its exterior with a thin layer of mercury. The conduction and radiation of heat are thus reduced to a minimum.

The critical temperatures (T) and critical pressures in atmospheres (P) of the gases condensed with difficulty are as follows:

	T	P
Carbon Dioxide, CO_2, ...	+ 31°	77 atmos.
Ethylene, C_2H_4, ...	+ 10°	51 "
Nitric Oxide, NO, ...	— 93°	71 "
Marsh Gas, CH_4, ...	— 82°	55 "
Oxygen, O_2, ...	—118°	50 "
Carbon Monoxide, CO, ...	—140°	35 "
Nitrogen, N_2, ...	—146°	35 "
Hydrogen, H_2, ...	—220°	15 "
Air, ...	—140°	39 "

Low temperatures are ascertained by means of a hydrogen or helium thermometer, a thermo-electric element composed of copper and German silver, or a platinum resistance thermometer.

The critical temperature, pressure and volume can be determined not only experimentally, but also may be deduced from the variations of the gases from the laws of Boyle and Gay-Lussac, by a theory developed by van der Waals (1873) (compare Air: measurement of gases). Students of chemistry desiring more detailed information on this subject are directed to the works of Ostwald: Grundriss der allgemeinen Chemie, 2 Aufl. 1890, and Lothar Meyer: Chemical Theories, 1893, and also Ostwald's Lehrbuch, vol. 1, 289 (1891).

HALOGEN GROUP.

Chlorine, bromine, iodine, and fluorine constitute this group. These elements show a similar chemical deportment. They are termed *halogens* or *salt producers*, because by their direct union with the metals salt-like derivatives result. Chlorine, bromine, and iodine will be discussed first because of their great importance.

1. CHLORINE.

Atom: $Cl = 35.45$. Molecule: $Cl_2 = 70.90$.

It does not occur free in nature. As it acts very energetically upon most bodies containing hydrogen, especially those of an organic nature, to form new derivatives with them or with their constituents, chlorine can only be obtained free in the transitional state. Its most important derivative is sodium chloride, or rock salt, which is composed of chlorine and sodium. The Swedish chemist, Scheele, discovered chlorine in 1774. It was regarded as a compound body, until its elementary character was established by Gay-Lussac and Thénard in France (1809), and by Davy in England (1810).

Preparation.—To obtain free chlorine, heat a mixture of black oxide of manganese (MnO_2) and hydrochloric acid in a flask (Fig. 31), provided with a so-called Welter safety-tube to equalize the gas pressure. The escaping gaseous chlorine is washed and freed from acid that is carried along mechanically by passing it through water in a three-necked Woulff bottle, and then collecting it over water. The reaction which occurs above is indicated in the following equation:

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The manganous chloride formed dissolves in the water.

At low temperatures the manganese peroxide dissolves in the hydrochloric acid without the evolution of chlorine, the solution being brown in color:

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O.$$

Chlorine is expelled on the application of heat:

$$MnCl_4 = MnCl_2 + Cl_2.$$

The evolution of the chlorine proceeds more regularly if a mixture of manganese oxide, sodium chloride, and sulphuric acid is employed.

The hydrochloric acid is formed from the last two (together with sodium acid sulphate):

$$NaCl + H_2SO_4 = HCl + NaHSO_4,$$

and then acts upon the manganese peroxide. It is advisable to use 5 parts of manganese peroxide (90 per cent.), 11 parts of sodium chloride, and 14 parts of concentrated sulphuric acid diluted with 7.5 parts of water [Klason, Ber. 23 (1890), 330].

The second method is more advantageous for laboratory purposes; the first (action of hydrochloric acid upon manganese dioxide), however, is preferred in practice, as it is cheaper.

The resulting manganous chloride ($MnCl_2$) is converted by the *process of Weldon* into manganese peroxide (see this).

Other technical methods for the preparation of chlorine are based upon the liberation of chlorine from hydrochloric acid or metallic chlorides (particularly calcium chloride and magnesium chloride) by the oxygen of the air at elevated temperatures. By-products of the soda industry, mother liquors of sea salt and tailings from the Stassfurth mines, all of which contain chlorine, are utilized in this way.

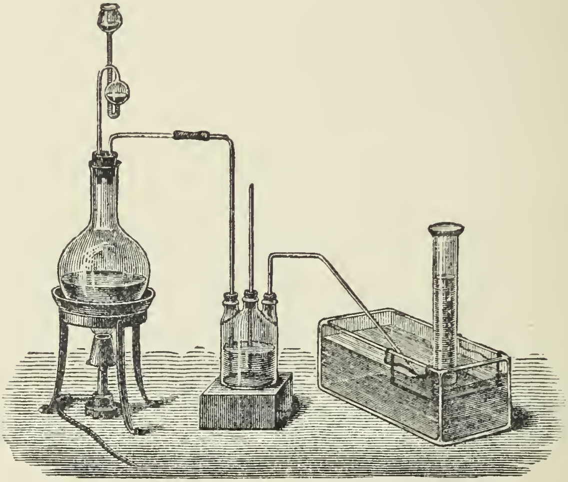


FIG. 31.

1. *Deacon-Hurter Process:* Hydrochloric acid mixed with air is conducted over porous substances saturated with copper chloride or sulphate and heated to 370–400°.

2. *Weldon-Pechiney Process:* Magnesium chloride or oxychloride is heated to 1000° in an air current: $MgCl_2 + O = MgO + Cl_2$; the magnesia is reconverted into chloride by solution in hydrochloric acid.

3. *Solvay Process:* Calcium chloride or magnesium chloride, mixed with silica or clay, is heated in an air current: $CaCl_2 + SiO_2 + O = CaOSiO_2 + Cl_2$.

4. *Reychler-de Wilde Method:* A mixture of magnesium chloride, manganous chloride and manganese sulphate is exposed to air heated to about 520° until the evolution of chlorine ceases, when it is restored by hydrochloric acid to its original condition and chlorine again liberated.

5. *Mond Method:* Ammonium chloride vapor is allowed to act upon magnesium oxide or other metallic oxides and the products are ammonia and metallic chlorides. The latter are heated to a high temperature in air when chlorine and oxides result.

The electrolytic decomposition of salt solutions is especially important; indeed it is likely to supplant the other technical processes in the near future. The current decomposes sodium chloride (and other metallic chlorides) into its components, so that chlorine separates at the positive and sodium at the negative pole. The sodium at once acts upon water forming sodium hydroxide and hydrogen. This universally important process will be again referred to in connection with soda, potassium chlorate and bleaching lime.*

An excellent laboratory method for the preparation of chlorine consists in allowing dilute hydrochloric acid to act upon bleaching lime (see this). The latter is previously mixed with burnt gypsum (¼ part), and a little water added, when the mass can be formed into cubes or stout sticks which are introduced into a Kipp generator (p. 42).

Very pure chlorine may be obtained by digesting potassium bichromate with concentrated hydrochloric acid:

$$K_2Cr_2O_7 + 14HCl = Cr_2Cl_6 + 2KCl + 7H_2O + 3Cl_2.$$

As chlorine dissolves readily in cold water it is advisable to collect it over warm water. It cannot be collected over mercury, as it readily combines with the latter. When perfectly dry chlorine is sought, conduct the liberated gas through Woulff bottles containing concentrated sulphuric acid, to absorb the moisture, then collect in an empty upright flask. As chlorine is so much heavier than air it will displace the latter.

Physical Properties.—Chlorine is a yellowish-green gas (hence its name from χλωρὸς), with a penetrating, suffocating odor. Its specific gravity compared with oxygen ($O_2 = 32$) is 70.9; with air (= 1) it is 2.45. A liter of chlorine at 0° and 760 mm. pressure at the sea-level in the latitude of 45° weighs 3.167 grams. At 15° C., and a pressure of 57 atmospheres (at —40° C., under the ordinary pressure) it condenses to a yellow liquid, boiling at —33 6°. By pressure and cold, liquid chlorine has been made applicable in technical operations (see Knietsch, Ann. Chem. **259** (1890), 100). The specific gravity of liquid chlorine at its boiling point is 1.5575. At very low temperatures it solidifies to a yellow crystalline mass, which remelts at —102°. The critical temperature of chlorine is 146°, and its critical pressure 93.5 atmospheres. It may be condensed in the following manner as demonstrated by Faraday: Take a bent glass tube (Fig. 32), introduce into the leg closed at one end crystals of chlorine hydrate ($Cl_2 + 8H_2O$, see p. 52), then seal the open end. The limb containing the compound is

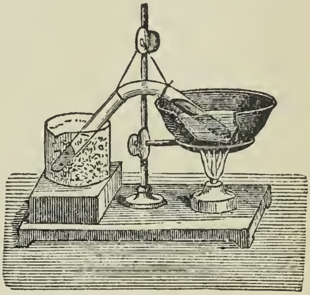


FIG. 32.

---

* Compare N. Caro, Darstellung von Chlor und Salzsäure, Berlin, 1893; also L. Mond, Geschichtlicher Ueberblick der verschiedenen Arten der Chlordarstellung, Chemiker-Zeitung, 1896, 928, and R. Hasenclever, Die Entwickelung der Sodafabrikation, Ber. **29** (1896), III, 2861.

placed in a water-bath; the other is cooled in snow. Upon heating the water a little above 30° the chlorine hydrate is decomposed into water and chlorine gas, which condenses to a liquid in the cooled limb. On reversing the position of the limbs and cooling the one previously warmed, the chlorine distils back and is reabsorbed by the water. Charcoal saturated with chlorine may be substituted for the chlorine hydrate. One volume of charcoal takes up 200 volumes of chlorine, which are disengaged again on heating.

One volume of water, at 20° C., absorbs 2 volumes of chlorine; at 10° C., 2.5 volumes. The aqueous solution is known as chlorine water (*aqua chlorata*), and possesses almost all the properties of the free gas; it is therefore frequently employed for laboratory uses as a substitute for chlorine.

Recent investigations show that chlorine water, by virtue of the action of the chlorine upon water, contains hydrochloric and hypochlorous acids, which in turn react upon one another with the production of chlorine and water, so that in accordance with the strength of the chlorine water and external prevailing conditions equilibrium occurs among these four substances (p. 29). This may be expressed as follows:

$$Cl_2 + H_2O \rightleftarrows HCl + HClO.$$

The yellow, scale-like crystals of chlorine hydrate ($Cl_2 + 8H_2O$) separate when water saturated with the gas is cooled below 0°. This compound is regarded as one of chlorine with water. At ordinary temperatures it decomposes into water and chlorine.

Chemical Properties.—When thin sheet copper (false gold leaf), or, better, pulverized antimony or arsenic, is thrown into a vessel filled with dry chlorine, it will burn with a bright light; a piece of phosphorus will also inflame in an atmosphere of the gas. Perfectly dry chlorine does not manifest this energetic combination-tendency.

Chlorine unites just as energetically with hydrogen. A mixture of equal volumes of the gases obtained by the electrolysis of hydrochloric acid combines in direct sunlight with violent explosion. In diffused sunlight the action is only gradual; in the dark it does not occur if perfectly dry gases are employed (Baker). The course of this reaction and the laws of the chemical action of light have been ably discussed in a series of celebrated papers by Bunsen and Roscoe [Pogg. Ann. d. Physik, Bd. **100, 101, 108** (1857–1859)]. Chlorine also manifests great affinity for hydrogen derivatives, most of them being so decomposed by the chlorine that hydrogen is removed from them, and hydrochloric acid is formed. Thus water is decomposed, especially in sunlight, by chlorine into hydrochloric acid and oxygen:

$$H_2O + Cl_2 = 2HCl + O.$$

If a glass cylinder be filled with and inverted over chlorine water and exposed to direct sunlight, a gas will be evolved, and will collect in the upper portion of the vessel; this is oxygen. In diffused light the decomposition will not be so rapid; it is hastened by heat. Chlorine oxygen acids, $HClO$, $HClO_3$ (see above), are also produced.

Chlorine alters the hydrocarbons, in that it abstracts hydrogen. The reaction is sometimes so violent that carbon is separated in a free condition. A piece of tissue paper saturated with freshly distilled turpentine oil, and introduced into a dry chlorine atmosphere, is immediately carbonized. An ignited wax taper immersed in chlorine burns with a smoky flame, with separation of carbon.

The organic dyestuffs (containing carbon and hydrogen) are decolorized by moist chlorine gas. The same occurs with the dark-blue solutions of indigo and litmus; colored flowers are rapidly bleached by it. On this principle depends the application of chlorine in bleaching, and the destruction of decaying matter and miasmata in chlorine disinfection are dependent upon this reaction (see Bleaching Lime).

The bleaching action of chlorine is mostly influenced by the presence of water. It probably depends on the oxidizing action of the oxygen liberated by the chlorine or upon the chlorine oxy-acids found when chlorine and water react (see p. 52). This property, free oxygen does not possess; it does, however, very probably belong to that which is in the act of forming,—of becoming free. We will learn, later, that many other elements, at the moment of their birth (*in statu nascendi*), act more energetically than when in the free condition.

2. BROMINE.

Atom: $Br = 79.96$. Molecule: $Br_2 = 159.92$.

Bromine, the perfect analogue of chlorine, was discovered by Balard, in 1826. It is not found free in nature for the same reasons which were given under chlorine. It occurs in sea-water as sodium bromide, accompanied by sodium chloride, but in much smaller quantity than the latter (especially in the water of the Dead Sea), and in many salt springs, as at Kreuznach and in Hall. When sea-water or other salt water is evaporated, sodium chloride first separates; in the mother liquor, among other soluble salts, are found sodium and magnesium bromides. Bromine is found in greatest abundance in the upper layers of the rock-salt deposits of Stassfurth, near Magdeburg, where it exists in the form of bromides together with other salts. At present, large quantities of bromine are obtained in America. The method of its preparation is similar to that employed under chlorine. A mixture of manganese dioxide and sodium bromide is warmed with sulphuric acid:

$$MnO_2 + 2NaBr + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + Br_2 + 2H_2O.$$

The bromine condenses in the well-cooled receivers. When free chlorine is conducted into an aqueous solution of sodium bromide, bromine separates. This is the method adopted at Stassfurth and in America in preparing bromine from the magnesium bromide saline liquors:

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

Bromine is a heavy, reddish-brown liquid, with an exceedingly penetrating, chlorine-like odor (hence the name Bromine, from βρῶμος, stench). When bromine is strongly cooled it solidifies to a dark-brown mass, of delicate needles with a slightly black metallic luster, which remelt at —7.3°. Liquid bromine at 0° has the specific gravity 3.18 (water = 1); it is very volatile, forming dark-brown vapors at the ordinary temperature, and boils at about 60°, changing at the same time into a dark brown-red vapor. Its density equals 159.9 (oxygen = 32), or 5.52 (air = 1).

One part of bromine dissolves in about 35 parts of water of medium temperature; it is therefore more soluble in water than chlorine. Cooled below 4° C., the hydrate ($Br_2 + 10H_2O$) crystallizes out: this is analogous to the chlorine hydrate. It is decomposed at 6.2°. Bromine dissolves with ease in alcohol, and especially in ether, chloroform and bisulphide.

Chemically, bromine is extremely like chlorine, combining directly with most metals to form bromides; but it possesses a weaker affinity than chlorine, and is liberated by the latter from its compounds. With hydrogen it only combines on warming, not in sunlight. Upon hydrocarbons it acts like chlorine, withdrawing hydrogen from them. Bromine water gives starch-paste an orange color.

Solid bromine is a mixture of liquid bromine with silicious earth. It occurs in trade pressed into cubes or sticks and is used for disinfecting purposes. Bromine and its salts are applied in medicine, in photography and in the manufacture of aniline colors.

3. IODINE.

Atom: $I = 126.85$. Molecule: $I_2 = 253.70$.

Iodine, as well as bromine, occurs in combination with sodium, in sea-water and some mineral springs, especially at Hall, in Austria, and the Adelheit spring in Bavaria. In these springs the iodine can easily be detected; in sea-water it is, however, only present in such minute quantity that its separation, practically, is disadvantageous. Sea algæ absorb iodine compounds from the water, and these are then thrown by the tide on various coasts, where they are burned, yielding an ash (known as *kelp* in Scotland, as *varec* in Normandy) which is the principal source for the manufacture of iodine. It was in this ash that the element was accidentally discovered by Courtois in 1811; in 1813, it was investigated by Davy and Gay-Lussac, and its elementary character established. To obtain the iodine, the ash is treated with water, the solution concentrated, and separated from the chlorides of sodium and potassium which have crystallized out, the final liquors, in which the readily soluble iodides have accumulated, being then distilled with manganese dioxide and sulphuric acid. Iodine, therefore, is set free from its compounds in the same manner as chlorine and bromine. It is more convenient, however, to pass chlorine (or better, nitrous acid) through a solution of the iodides, when all the iodine will separate:

$$KI + Cl = KCl + I,$$

or the iodide solution is digested with ferric chloride, when the latter is reduced to ferrous chloride:

$$NaI + FeCl_3 = I + NaCl + FeCl_2.$$

The grayish-black powder thus liberated is collected on a filter, dried, and then sublimed.

In recent years the greatest quantities of iodine have been obtained from the mother liquors of crude Chile saltpeter ($NaNO_3$). The iodine is present in this salt as sodium iodate ($NaIO_3$), from which it is set free by nitrous or sulphurous acid :

$$2NaIO_3 + 5H_2SO_3 = 2I + 2NaHSO_4 + 3H_2SO_4 + H_2O.$$

An interesting occurrence of iodine is that observed by Baumann in 1895 in the thyroid (thyroidea, from θυρεός, shield, and εἶδος, form) gland, the active constituent of which, containing 9 per cent. of iodine, is mixed with milk-sugar and sold in the markets under the name *thyroidin.*

Iodine is a gray-black solid, subliming in large rhombic crystals, possessing strong metallic luster. It has a peculiar odor, reminding one somewhat of that of chlorine; it stains the skin brown, and is corrosive, although not as strongly so as bromine. Its specific gravity is 4.95 at 15°. It fuses at 114° to a dark-brown liquid, and boils near 184.3°, passing at the same time into a dark-violet vapor (hence the name Iodine, suggested by Gay-Lussac, from ἰοειδής, violet-like).

The vapor density of iodine equals 8.7 up to 600° C. (air = 1) or 254 ($O_2 = 32$), corresponding to the molecular weight $I_2 = 253.7$. Above 600° the vapor density gradually diminishes, and at about 1500° it is only half the original. This is explained by the gradual decomposition (see Dissociation of Water) of the normal diatomic molecule I_2 into the free atoms $I + I$. In like manner the bromine molecules Br_2 suffer a separation into the free atoms. The dissociation of bromine vapor (diluted with 11 volumes of nitrogen) commences at about 1000° and is complete at 1600°. The vapor density of chlorine is still normal at 1200°, and it is only at 1400° that it sustains a slight diminution. Oxygen and nitrogen on the contrary show no alteration in their vapor density even at 1690° (C. Langer and V. Meyer).

Iodine is very slightly soluble in water (1 : 3600), more readily in alcohol (*Tinctura iodi*), very easily in aqueous potassium iodide, in ether, in chloroform and in carbon bisulphide (10 c.c. of the latter will dissolve 1.85 grams of iodine at 18°), the last two assuming a deep red-violet color in consequence. It affords a particularly beautiful crystallization, consisting of forms of the rhombic system, when it separates from a solution of glacial acetic acid.

In chemical deportment iodine closely resembles bromine and chlorine; it possesses, however, weaker affinities and for this reason is liberated from its compounds by those elements. With the metals it usually combines only when warmed; with hydrogen it does not combine directly, and it does not remove it from its carbon compounds.

The deep-blue color it imparts to starch is characteristic of iodine. On adding starch-paste to the solution of an iodide, and following this with a few drops of chlorine water, the paste will immediately be colored a dark blue by the separated iodine. This reaction serves to detect the smallest quantity of it.

Iodine is largely employed in medicine, photography, and in the preparation of aniline colors.

4. FLUORINE.

Atom: Fl = 19. Molecule: Fl_2 = 38.

Fluorine has such great affinity for nearly all substances, that despite numerous efforts it has only recently been possible to obtain it in a free condition. It was Moissan (1886) who electrolyzed anhydrous, strongly chilled hydrofluoric acid to which some sodium fluoride had been added, and obtained fluorine as a slightly greenish-yellow colored gas. The decomposing vessel was a platinum tube with stoppers of fluorspar. The positive pole, at which the fluorine appeared, consisted of an alloy of platinum and iridium. Dewar and Moissan have very recently succeeded in liquefying fluorine at —187° by the use of boiling oxygen as the refrigerating substance. Under these conditions it loses its chemical activity almost completely, does not attack glass, iodine, sulphur, or metals. It is only the affinity for hydrogen which remains; at least benzene is entirely decomposed with production of flame by fluorine.

Fluorspar ($CaFl_2$) is the most important fluorine derivative. It is most frequently employed in the preparation of other fluorine compounds.

Fluorine combines with hydrogen, iodine, sulphur, silicon, boron, powdered arsenic and antimony, finely divided iron and manganese even in the dark; organic substances, like oil of turpentine, alcohol and cork burn in the gas. The metals, with the exception of gold and platinum, are energetically attacked by fluorine. The latter decomposes water with the production of hydrofluoric acid and ozonized oxygen, and liberates chlorine, bromine and iodine from their metallic derivatives. The density of fluorine referred to hydrogen equals 1.32 (1.26 found).

These four elements, fluorine, chlorine, bromine and iodine, exhibit gradual differences in their properties; and, what is remarkable, this gradation stands in direct relation to the specific gravity of the elements in the state of gas or vapor.

	Fl	Cl	Br	I
Specific gravity,	19	35.45	79.96	126.85

A simultaneous condensation of matter occurs with the increase of specific gravity. This expresses itself in the diminished volatility. Fluorine is a gas down to —187°; chlorine can readily be condensed to a liquid; bromide is a liquid at ordinary temperatures, and iodine is a solid. Other physical properties, as seen in the following table, are also in accord with the preceding:

	FLUORINE.	CHLORINE.	BROMINE.	IODINE.
Fusing point, ...	. . . .	—102°	—72°	+114°
Boiling point, ...	—187° (?)	— 33°	+60°	+184°
Specific gravity in liquid	1.14	1.47	3.18	. . . .
or solid condition, ...	. . . .	. . . .	. . . .	4.95
Color, ...	Green-yellow	Yellow-green	Brown	Black-violet

Just such a gradation, as we have seen, is observed in the chemical affinities of these four elements for the metals and hydrogen ; fluorine is the most energetic, iodine the least. Iodine is therefore separated from its soluble metallic and hydrogen compounds by the other three, bromine by chlorine and fluorine, and chlorine by fluorine (p. 56). We shall discover, later, that the halogens are displaced in exactly the reverse order of their oxygen compounds; that iodine has the greatest and chlorine the feeblest affinity for oxygen. Oxygen derivatives of fluorine are not known.

COMPOUNDS OF THE HALOGENS WITH HYDROGEN.

The halogens form gaseous acids, readily soluble in water, with hydrogen : the halogen hydrides or haloid acids. But one such compound is known for each halogen.

1. HYDROGEN CHLORIDE.

$HCl = 36.46$.

The direct union of chlorine with hydrogen takes place through the agency of heat, and by the action of direct sunlight or other chemically active rays (magnesium light); in diffused light the action is only gradual, and does not occur at all in the dark. When both gases are perfectly dry they do not react in direct sunlight. On introducing a flame of hydrogen ignited in the air into a cylinder filled with chlorine it will continue to burn in the latter with the production of hydrogen chloride. The opposite, the combustion of chlorine in an atmosphere of hydrogen, may be shown easily by the following experiment : An inverted cylinder is filled with hydrogen by displacement, the gas is ignited at the mouth, and a tube immediately introduced which will conduct dry chlorine into the cylinder. The burning hydrogen will inflame the chlorine, which will continue to burn in the former. From these experiments, we perceive that combustion is a phenomenon which accompanies a chemical change; in this instance the union of hydrogen with chlorine; if hydrogen is combustible in chlorine (or air), so, inversely, is chlorine (or air) combustible in hydrogen for the same reason. By the term combustion, in chemistry, is understood every chemical union of a body with a gas, which is accompanied by the phenomenon of light.

A mixture of equal volumes of chlorine and hydrogen is called *chlor-detonating gas ;* it explodes with very great violence under the conditions given above for the union of the gases. The product is gaseous hydrogen chloride.

The formation of the latter compound succeeds best by allowing sulphuric acid to act upon sodium chloride when solid sodium bisulphate and hydrogen chloride gas will result:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

Pour over 5 parts sodium chloride, 9 parts of concentrated sulphuric acid, diluted with water (2 parts), and gently warm the flask on a sand-bath (Fig. 33). The escaping hydrogen chloride is conducted through a Woulff bottle containing sulphuric acid or through the cylinder B (filled with pumice-stone saturated with sulphuric acid), intended to free it from all moisture, and afterward collected over mercury in the cylinder C.

At a red heat, the acid sodium sulphate reacts anew upon the sodium chloride with the formation of neutral sodium sulphate and hydrochloric acid:

$$NaHSO_4 + NaCl = HCl + Na_2SO_4.$$

These are the reactions by which hydrochloric acid, in the preparation of sodium sulphate by the Le Blanc soda process, is technically made. As this method, however, is being replaced by the electrolytic method, in which not hydrochloric acid, but chlorine is evolved, it seems very important that the latter should be converted by some convenient procedure into hydrochloric acid, always of the greatest importance technically. Lorenz contends that this may be accomplished by conducting the chlorine together with steam over ignited coke, when the chief products will be hydrochloric acid and carbon dioxide (CO_2):

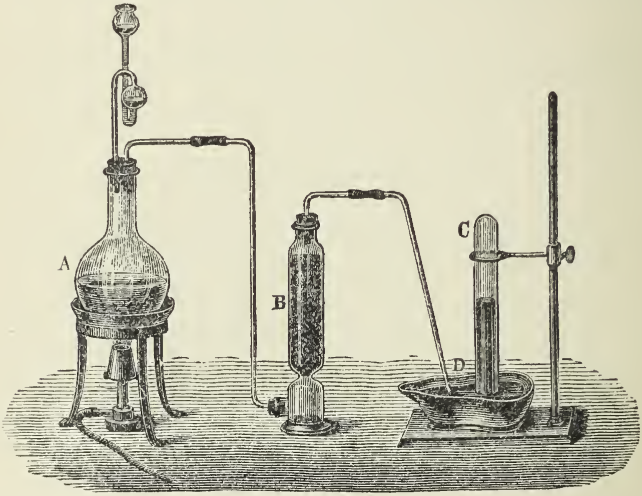


FIG. 33.

$$2Cl_2 + 2H_2O + C = 4HCl + CO_2.$$

[Compare Ber. 30 (1897), 1, 347].

The suggestion of Davy to allow sulphuric acid to act upon pieces of ammonium chloride will give a regular current of hydrogen chloride:

$$NH_4Cl + H_2SO_4 = (NH_4)HSO_4 + HCl.$$

A Norblad generator as modified by Kreussler (Fig. 34) answers well for this purpose.

Physical Properties.—Hydrogen chloride is a colorless gas, with a suffocating odor. In moist air it forms dense clouds as it combines with the aqueous vapor to form hydrochloric acid. Its critical temperature is about +52.3°, and the critical pressure 86 atmospheres, *i. e.*, for its condensation at the temperature just given it requires a pressure of 86 atmospheres. There is no pressure which will condense it above this temperature. Liquid hydrogen chloride is colorless, has a specific gravity at 15° of 0 83, and freezes at —115.7° to a white crystalline mass, which begins to melt at —112.5°. It boils at —80.3° under the ordinary pressure.

The specific gravity (density) of the gas is 36.46 ($O_2 = 32$), or 1.26 (air = 1). One liter of it weighs 1.6285 grams at 0°, 760 mm. pressure, in latitude 45° and at sea-level.

Hydrogen chloride possesses an acid taste, and colors in the presence of water blue litmus-paper red; it is, therefore, an acid, and has received the name hydrochloric acid gas. It dissolves very readily in water, and on that account cannot be collected over it. One volume of water at 0° C. and 760 mm. pressure dissolves 505 volumes, and at ordinary temperatures about 450 volumes of the gas. At higher pressure water dissolves more hydrochloric acid, and at low pressures less (compare Carbon Dioxide, and also Solutions). This great solubility is very nicely illustrated by filling a long glass cylinder with the gas and then just dipping its open end into water; the latter rushes up into the vessel rapidly (as into a vacuum), as it quickly absorbs the gas. The aqueous solution of hydrogen chloride is commonly known as muriatic or hydrochloric acid (*Acidum hydrochloricum*). For its preparation the gas is passed through a series of Woulff bottles (Fig. 35) containing water. The small bottle *B*, in which there is but little water, serves to wash the gas—free it of any mechanically admixed sulphuric acid. The same apparatus may be employed in the manufacture of chlorine water, and is generally used in the saturation of liquids with gases.

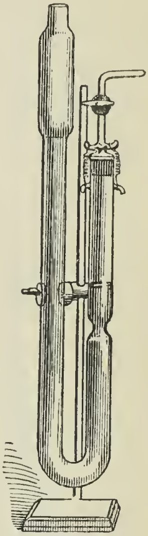


FIG. 34.

A solution saturated at 15° C., contains about 42.9 per cent. hydrogen chloride, has a specific gravity of 1.212, and fumes in the air. On the application of heat, the gas again escapes, and the temperature of the liquid rises to 110° C., when a liquid distils over, containing 20.24 per cent. of hydrogen chloride, having a specific gravity of 1.104 and corresponds approximately to the formula $HCl + 8H_2O$. The composition of the distillate varies somewhat with the pressure. A dilute acid, upon distillation, loses water, until finally that boiling at 110° C. passes over. On conducting hydrogen chloride into concentrated hydrochloric acid cooled to —22°, crystals of the formula $HCl + 2H_2O$ separate; these fuse at —18° and then decompose.

Hydrochloric acid finds an extensive industrial application, and is obtained in large quantities, as a by-product, in the soda manufacture (Le Blanc process).

Chemical Properties of Hydrogen Chloride.—Acids—Bases—Salts.—Hydrogen chloride is a very stable compound; it is only beyond 1500° that it sustains a partial decomposition (see Dissociation of Water). Its composition is readily established quantitatively in the following way: Pass hydrochloric acid gas over a piece of sodium or potassium heated in a glass tube, and hydrogen will escape from the latter: $2Na + 2HCl = 2NaCl + H_2$. If, on the other hand, manganese peroxide be heated in it, chlorine will be disengaged: $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$. If the electric current be allowed to act upon an aqueous solution of hydrochloric acid the latter will be decomposed so that chlorine separates at the electro-positive and hydrogen at the electro-negative pole (p. 77). Hydrogen chloride, as well as its solution, possesses all the properties of *acids*, and can well figure as a prototype of these; it tastes intensely sour, reddens blue litmus-paper, and saturates the *bases* (oxides and hydroxides, *i. e.*, which bodies impart a blue color to red litmus-paper) forming chlorides. There are some bases, the alkalies and alkaline earths, which are soluble in water. These solutions react *basic*, *alkaline*, *i. e.*, red litmus is colored blue by them. If we add hydrochloric acid to a solution of a base, *e. g.*, sodium hydroxide, until the reaction is neutral, we will obtain (besides water) a neutral compound—sodium chloride, which remains in a crystalline form when the solution is evaporated:

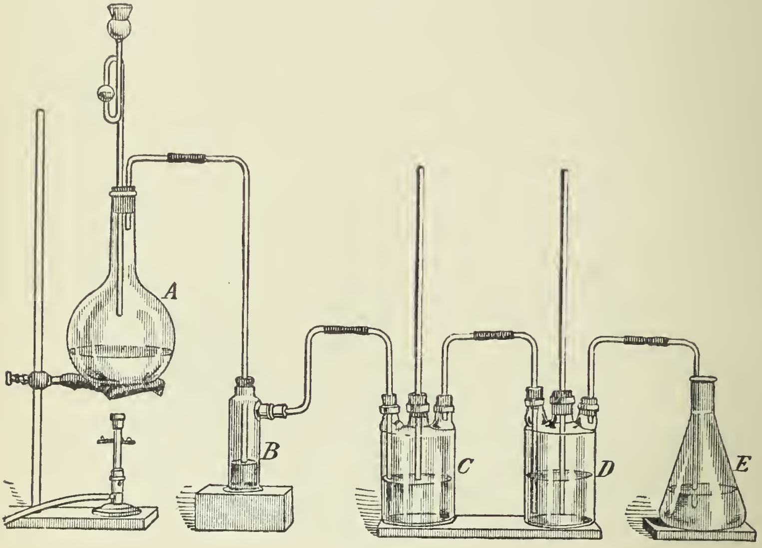


FIG. 35.

$$\underset{\text{Sodium hydroxide.}}{NaOH} + HCl = \underset{\text{Sodium chloride.}}{NaCl} + H_2O.$$

Hydrogen bromide, iodide and fluoride deport themselves similarly to hydrogen chloride. These halogen compounds of hydrogen are termed *haloid acids*, to distinguish them from those which, in addition to hydrogen, contain oxygen, hence called *oxygen acids*. The latter conduct themselves like the former, and saturate bases, forming salts and water:

$$\underset{\substack{\text{Potassium}\\\text{hydroxide.}}}{KOH} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{HNO_3} = \underset{\substack{\text{Potassium}\\\text{nitrate.}}}{KNO_3} + \underset{\text{Water.}}{H_2O}.$$

In the same manner the acids act upon the basic oxides, to form salts and water:

$$\underset{\substack{\text{Zinc}\\\text{oxide.}}}{ZnO} + 2HCl = \underset{\substack{\text{Zinc}\\\text{chloride.}}}{ZnCl_2} + H_2O.$$

$$\underset{\substack{\text{Zinc}\\\text{oxide.}}}{ZnO} + 2HNO_3 = \underset{\substack{\text{Zinc}\\\text{nitrate.}}}{Zn(NO_3)_2} + H_2O.$$

Usually when acids act upon metals, the hydrogen of the former is directly displaced; *salts* and free hydrogen are produced. Thus, by the action of hydrochloric acid upon sodium, its chloride and hydrogen result:

$$HCl + Na = NaCl + H;$$

and when zinc and hydrochloric acid react, zinc chloride and water (see p. 41):

$$2HCl + Zn = ZnCl_2 + H_2.$$

From the examples cited it is manifest that *acids* are hydrogen compounds which yield *salts*, by the replacement of their hydrogen by metals (by the action of metallic oxides, hydroxides, and by the free metals). The metallic oxides and hydroxides like sodium hydroxide, capable of forming water and salts by the saturation of acids, are called *bases*. Finally, by the term *salts*, we understand such compounds as are analogous to sodium chloride, and are formed by the mutual action of bases and acids with the exit of water. Salts are distinguished as *haloid salts* and *oxygen salts*. The first have no oxygen, and arise in the direct union of the halogens with the metals:

$$Na + Cl = NaCl.$$
$$Zn + Cl_2 = ZnCl_2.$$

2. HYDROGEN BROMIDE.

$HBr = 80.97$.

Hydrogen bromide is perfectly similar to the corresponding chlorine compound. As there is but slight affinity between bromine and hydrogen their direct union will only occur at a red heat or in the presence of platinum sponge (see p. 46). Like hydrogen chloride, hydrogen bromide can be obtained by the action of some acids, *e. g*, phosphoric acid, upon bromides; concentrated sulphuric acid would not answer as the resulting hydrogen bromide is again partly decomposed by it. Ordinarily it is prepared by the action of phosphorus tribromide upon water:

$$\underset{\text{Phosphorus tribromide.}}{PBr_3} + 3H_2O = \underset{\text{Phosphorous acid.}}{H_3PO_3} + 3HBr.$$

Place water (1 part) in a flask (Fig. 36), gradually admit through the funnel, supplied with a stop-cock, the liquid phosphorus tribromide (3 parts), and warm gently. The escaping gas is collected over mercury or conducted into water. To free it perfectly from accompanying phosphorus bromide vapors it is passed through water (the U-shaped tube in Fig. 36 contains pieces of pumice-stone or glass beads, which are moistened with water).

Instead of employing prepared phosphorus bromide, we may let bromine vapors act upon (red) phosphorus. This may be done by pouring water (2 parts) over the phosphorus placed in a flask; Bromine (10 parts) is added gradually while cooling and heat is then applied. To free the hydrogen bromide gas from the bromine carried along mechanically, conduct it through a tube containing glass wool and moist red phosphorus.

Gaseous hydrobromic acid can also be prepared by allowing bromine to act upon crude anthracene. The resulting hydrobromic acid gas is freed from the accompanying bromine by passing it through a tube filled with anthracene.

To obtain an aqueous solution of the gas, pour 15 parts of water over 1 part of red phosphorus, and then add bromine (10 parts) drop by drop. Finally the solution is heated, filtered, and distilled. Bromides (sodium bromide, potassium bromide) yield hydrogen bromide by distillation with dilute sulphuric acid in the presence of phosphorus.

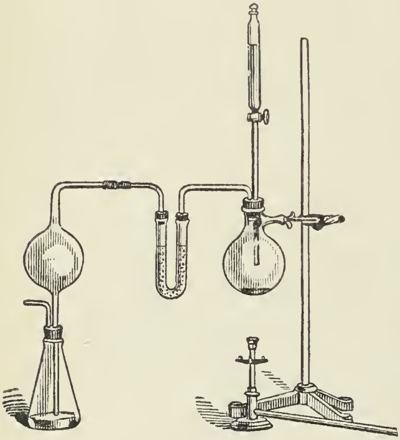


FIG. 36.

Hydrogen bromide is a colorless gas, fuming strongly in the air. Under great pressure it is condensed to a liquid, solidifying at —120°, melting at —87°, and boiling at —73°. Its density is 80.97 ($O_2 = 32$) or 2.79 (air = 1).

In water the gas is very readily soluble, its solution saturated at 0° having a specific gravity of 1.78, and containing 82 per cent. of hydrogen bromide. Its composition closely approximates the formula $HBr + H_2O$; at 15° it contains 49.8 per cent. of acid and has the specific gravity 1.515. At 125° a solution distils over, containing 48.2 per cent. of hydrogen bromide; its composition corresponds very nearly to the formula $HBr + 5H_2O$; its specific gravity is 1.49 at 14° C.

On conducting hydrogen bromide into a solution of the same cooled to —20°, crystals of the formula $HBr + 2H_2O$ separate and melt at —11°. Chemically, hydrogen bromide is the perfect analogue of hydrogen chloride; it is, however, less stable, and suffers a partial decomposition at 800° C.

3. HYDROGEN IODIDE.

$HI = 127.86$.

The attraction of iodine for hydrogen is very slight. The two elements combine at higher temperatures, between 400 and 500°, very incompletely with one another, because at this point hydrogen iodide is partly resolved into its elements (see below). Their union is more complete if both elements, in the form of vapor, are conducted over heated platinum sponge. It cannot be obtained by acting upon iodides with sulphuric acid, because the resulting hydrogen iodide decomposes more easily than the bromide. It is formed, however, similarly to the latter, by acting on phosphorus iodide with water:

$$PI_3 + 3H_2O = H_3PO_3 + 3\ HI.$$

A more convenient procedure consists in adding 15 parts of iodine (to which 10 parts of water have been added) gradually and while cooling to a mixture of one part of red phosphorus and four parts of water, and then gently heat the same; or allow an emulsion of red phosphorus (5 parts) with water (10 parts) to flow gradually and at first very slowly upon iodine (100 parts) moistened with water (10 parts) (Lothar Meyer, Ber. 20 (1887), 3381). Hydrogen iodide prepared in this way is invariably contaminated with phosphorus compounds. The pure gas can only be made by the method mentioned above: by conducting iodine vapor and hydrogen over heated platinum sponge. Water is then saturated with the escaping gas and on heating this fuming hydriodic acid a steady current of hydrogen iodide is easily obtained. It is dried by passing it over phosphorus pentoxide. (See Bodenstein, Zeit. f. phys. Ch. 13 (1894), 59.)

Another method of obtaining aqueous hydrogen iodide consists in passing hydrogen sulphide into water to which finely pulverized iodine is added, as long as decolorization occurs:

$$H_2S + I_2 = 2HI + S.$$

Filter off the separated sulphur and distil the liquid. Dry iodine and dry hydrogen sulphide do not react upon one another.

Hydrogen iodide is a colorless gas; it fumes strongly in the air; its density is 128 ($O_2 = 32$) or 4.4 (air = 1). Under a pressure of 4 atmospheres (at 0°) it is condensed to a liquid which boils at —34°.* It solidifies at lower temperatures and remelts at —51°. It is easily soluble in water, 1 volume of the latter dissolving 450 volumes of the gas at 10°. The solution saturated at 0° C., has a specific gravity of 1.99, and fumes strongly in the air. If the solution be heated hydrogen iodide is expelled, the temperature rises and at 126° a solution of 1.70 specific gravity, containing 57 per cent. of hydrogen iodide, distils over. Its composition corresponds closely to the formula $HI + 5H_2O$.

Hydrogen iodide is a rather unstable compound. Its decomposition takes place at all temperatures at which it exists as a gas; the speed of its disintegration increases rapidly with the temperature. While only the two-thousandth part of the hydrogen iodide separates into hydrogen and iodine in ninety days at a temperature of 100°, almost one-fourth of it

---

* Consult Estreicher, Zeit. f. phys. Ch., 20 (1896), 605, upon the behavior of hydrogen chloride, bromide and iodide at low temperatures.

will be decomposed in fifteen minutes at 518°, and the maximum decomposition for this temperature will then have been attained (see Dissociation of Water). At high temperatures oxygen decomposes into water and iodine:

$$2HI + O = H_2O + I_2.$$

On bringing a flame near the mouth of a vessel containing a mixture of hydrogen iodide and oxygen, violet iodine vapors will be liberated. The same will be noticed when fuming nitric acid is dropped into a vessel containing the gas; in this reaction the oxygen of the acid oxidizes the hydrogen and liberates iodine. The nitric acid breaks down into compounds containing less oxygen. All oxidizing bodies behave in the same way; the hydrogen iodide abstracts their oxygen and *reduces* them. The same fact is noticed with concentrated sulphuric acid when the attempt is made to apply it in liberating hydrogen iodide from an iodide. The oxygen of the air gradually decomposes aqueous hydrogen iodide at the ordinary temperature, and especially in sunlight. The solution, at first colorless, becomes brown, owing to separation of iodine, which in the beginning dissolves; subsequently, however, it separates in beautiful crystals.

At ordinary temperatures mercury and silver decompose hydrogen iodide, with separation of hydrogen:

$$2HI + 2Ag = 2AgI + H_2.$$

Chlorine and bromine liberate iodine from hydrogen iodide (see p. 54).

This compound is employed as a powerful reducing agent in laboratory work.

4. HYDROGEN FLUORIDE.

$HFl = 20.01.$

It is obtained, like hydrogen chloride, by decomposing fluorides with sulphuric acid. Finely pulverized fluors-par ($CaFl_2$) is mixed with concentrated sulphuric acid and heated gently:

$$\underset{\substack{\text{Calcium}\\\text{fluoride.}}}{CaFl_2} + H_2SO_4 = \underset{\substack{\text{Calcium}\\\text{sulphate.}}}{CaSO_4} + 2HFl.$$

The operation is executed in a lead or platinum retort, as the hydrogen fluoride attacks glass and most of the metals. The escaping gas is conducted into water. To get perfectly anhydrous hydrogen fluoride, heat hydrogen potassium fluoride, which then decomposes according to the following equation:

$$HKFl_2 = KFl + HFl.$$

Anhydrous hydrogen fluoride is a colorless, very mobile liquid, fuming strongly in the air, and attracting moisture with avidity; it boils at +19.4° C., and has a specific gravity of 0.98 at 12°. To recondense the gas it must be cooled to —20°. Hydrogen fluoride solidifies at —102.5° and remelts at —92.5°.

The gas density of hydrogen flouride equals 20.01 ($O_2 = 32$) at 100°, corresponding to the molecular formula HFl. At 30°, however, it is twice as large, equaling 40. It follows, therefore, that the molecules of the gas at the latter temperature correspond to the formula H_2Fl_2, and consist of two chemical molecules of HFl (compare Arsenic Trioxide).

The concentrated aqueous solution fumes in the air; when heated, hydrogen fluoride escapes; the boiling temperature increases regularly and becomes constant at 120°, when a solution distils over, the specific gravity of which is 1.15, and its percentage of hydrogen fluoride is 35.3. The vapors as well as the solution are poisonous, extremely corrosive, and produce painful wounds upon the skin.

Hydrofluoric acid dissolves all the metals, excepting lead, gold and platinum, to form fluorides. It decomposes all oxides, even the anhydrides of boric and silicic acids, which it dissolves to form boron and silicon fluorides. Glass, a silicate, is also acted upon; hence the use of the acid for etching this substance (compare Silicon Fluoride). To do this, coat the glass with a thin layer of wax or paraffin, draw any figure upon it with a pin, and then expose it to the action of the gaseous or liquid hydrogen fluoride. The exposed portions appear etched; gaseous hydrogen fluoride furnishes a dim, and liquid hydrogen fluoride a smooth, transparent etching.

Vessels of lead, platinum, or caoutchouc are employed for the preservation of hydrofluoric acid, as they are not affected by it.

These halogen derivatives of hydrogen show great resemblance to one another. At ordinary temperatures they form strongly smelling and fuming gases, which can be easily condensed to liquids. Their fuming in moist air is due to the fact that they are dissolved by the water vapor and the resulting solutions appear as a cloud consisting of very minute drops. Being readily soluble in water, they are only partly expelled from their saturated solutions by boiling; solutions of definite composition distil over, but these cannot be regarded as definite chemical combinations of the halogen hydrides with water, because their composition depends upon the pressure at which they are boiled (Roscoe).

As acids they neutralize the bases and form haloid salts, which also result by the direct union of the halogens with metals.

The densities of the halogen hydrides exhibit a gradation similar to that of the densities of the halogens (p. 56):

	HFl	HCl	HBr	HI
Densities,	20.01	36.46	80.97	127.86

The difference in chemical deportment corresponds to this gradation. Hydrogen fluoride is the most stable, and acts most energetically; fluorine unites in the dark with hydrogen; chlorine combines with it in sunlight, while bromine and iodine require higher temperatures for their combination with it. On the other hand, hydrogen iodide is decomposed at a gentle heat (180°), into its constituents; the more stable hydrogen bromide at 800°, while hydrogen chloride remains unaltered up to 1500° C.

Corresponding to this we have the very energetic action of fluorine, and the tolerably ready action of chlorine upon water, oxygen separating at the same time:

$$H_2O + Cl_2 = 2HCl + O.$$

Iodine does not act upon water. The opposite reaction occurs: oxygen decomposes hydrogen iodide into water and iodine:

$$2HI + O = H_2O + I_2.$$

Bromine occupies an intermediate position between chlorine and iodine; in dilute aqueous solution it decomposes water into hydrogen bromide and oxygen, while a concentrated solution of hydrogen bromide, on the contrary, is partly decomposed by oxygen into water and free bromine.

From all the above it is evident that the affinity of fluorine for hydrogen is the greatest; then follow chlorine and bromine, and finally, as the least energetic element, we have iodine (see p. 57). Fluorine holds an exceptional position with the other halogens in that its hydride is a liquid at the ordinary temperature, and many of its metallic derivatives show a solubility directly opposite to that of the metallic chlorides, bromides, and iodides. This will be discussed later.

THERMO-CHEMICAL DEPORTMENT OF THE HALOGENS.

The quantities of heat, disengaged or absorbed in chemical reactions, afford the most satisfactory explanations of the deportment of the halogens with hydrogen, and indeed of all the chemical elements and compounds toward one another. These heat changes are also called *positive* and *negative* thermal values (*heat modulus*) (see p. 30).

The quantities of heat are estimated in *heat units* or *calories*. The quantity of heat required to raise one gram of water 1° C. from 15° (measured with an air-thermometer), is taken as the *heat unit* (small calorie), or a thousand times this quantity can be taken; then it would be the quantity of heat needed to raise 1 kilogram of water from 15° to 16° (large calorie, Cal.). Large calories will be used in the following pages. (See further, Nernst, Theoretische Chemie, 2 Aufl. (1898), 10.)

To obtain data that may be easily compared, the quantities of heat are referred to quantities in grams corresponding to the atomic or molecular weights of the elements entering into combination. Thus, in the union of 19 grams of fluorine ($Fl = 19$) with 1.01 grams of hydrogen ($H = 1.01$) to form 20.01 grams of hydrogen fluoride ($HFl = 20.01$), 37.6 Cal. are set free, and in the formation of 36.46 grams of hydrogen chloride ($HCl = 36.46$) from its elements 22.0 Cal. When 79.96 grams of bromine ($Br = 79.96$) combine with 1.01 grams of hydrogen to form hydrogen bromide 8.4 Cal. are developed, while in the formation of 127.86 grams of hydrogen iodide from solid iodine and hydrogen 6.0 Cal. are absorbed, but with iodine vapor and hydrogen only 1.5 Cal. (4.5 Cal. being required for the vaporization of the given amount of iodine).

This may be expressed according to the method of J. Thomsen, as follows:

$$(H,Fl) = +37.6 \text{ Cal.}; \quad (H,Cl) = +22.0 \text{ Cal.}; \quad (H,Br) = +8.4 \text{ Cal.}; \quad (H,I) = -1.5 \text{ Cal.}$$

The first three reactions, in which heat is liberated, are *exothermic*, while the heat-absorbing combination of iodine with hydrogen represents an *endothermic* reaction (see p. 30). The energy-content of hydrogen fluoride, chloride and bromide is less, and that of hydrogen iodide greater than that of their components.

The quantity of heat disengaged in a combination must not be regarded as a measure of the chemical affinity. As the elements with few exceptions: see argon, helium, mercury, and cadmium—do not exist as free atoms, but as molecules these require a definite quantity of heat to decompose them into atoms before they can enter into chemical reaction. This necessitates a definite amount of work (addition of energy). The union of chlorine with hydrogen proceeds according to the molecular equation (p. 76):

$$HH + ClCl = 2HCl.$$

The heat here disengaged ($2 \times 22.0 = 44.0$ Cal.) is the algebraic sum of the following unknown thermal values: (1) —x Cal., required for the decomposition of the hydrogen molecule into free atoms; (2) —y Cal., consumed in the decomposition of the chlorine molecule; (3) +z Cal., liberated in the formation of hydrogen chloride from the free chlorine and hydrogen atoms; hence $z - x - y = 44.0$, *i. e.*, the thermal value is deduced from the three unknown values.

It is very probable that the union of the free atoms always occurs with heat-disengagement, and the heat-absorption, observed in many chemical changes, is to be credited to the decompositions to which attention has been directed. In the formation of hydrogen iodide, for example, the sum of —x and —y is very probably greater than z.

The greater the heat developed in a reaction, the more energetically and the more readily will it occur, and in general, the resulting compounds will be the more stable (compare p. 65, Behavior of the Halogen Hydrides). The energetic reactions, those which are accompanied by very appreciable evolution of heat, must be viewed as transitions of systems from a state of comparative instability to one of greater permanency. The opposite occurs if the chemical change only takes place upon the addition of external energy. The compound then produced passes very readily into the original and more stable system. In this sense the principle of greatest heat-development is true (p. 31).

In this way it can be understood from the thermal values of the halogen hydrides why it is that iodine is displaced by the other halogens, bromine by chlorine and fluorine and chlorine by fluorine from their hydrides and their metallic derivatives—corresponding to the following thermo-chemical equations:

$$\underset{(-6.0)}{HI} + Cl = \underset{(22.0)}{HCl} + I \quad \ldots \quad (+28 \text{ Cal.})$$

$$\underset{(8.4)}{HBr} + Cl = \underset{(22.0)}{HCl} + Br \quad \ldots \quad (+13.6 \text{ Cal.})$$

$$\underset{(22.0)}{HCl} + Fl = \underset{(37.6)}{HFl} + Cl \quad \ldots \quad (+15.6 \text{ Cal.})$$

The thermo-chemical sign of a reaction is obtained by deducting from the heat of formation of the products that of those reacting.

The reactions do not proceed wholly in the sense indicated. They are limited by accurately opposing forces. When bromine acts upon hydrochloric acid the transposition takes place, if even in a very slight degree, according to the equation Br + HCl =

$HBr + Cl$. And it must therefore be assumed from this equation that when chlorine acts upon hydrobromic acid a portion of the bromine liberated will transpose itself with the hydrogen chloride which has been formed: the reaction reverses itself, is retrogressive. To what extent this happens, to what degree of divisions these reactions, occurring simultaneously but proceeding in opposite directions, will go, depends upon the nature of the reacting bodies, the ratios of their quantities in unit volume, the temperature, the time, the pressure; and finally a state of equilibrium will be developed. The retrogressive reaction very frequently advances so slowly, consequently amounts to so little, that it may appear as if it actually did not occur at all.

These facts demonstrate that Berthelot's principle of the greatest heat development is not universally correct although it often indicates the direction in which a transformation occurs easily and completely. As an argument favoring this we have the different decomposability of the gaseous halogen hydrides by oxygen, taking into consideration, of course, the heat of formation of water. For aqueous vapor this is 57.2 Cal., while for the liquid it is 68.3 Cal. The union of 1 gram of hydrogen with 8 grams of oxygen is attended with a thermal value of $\frac{57.2}{2} = 28.6$ Cal., which is greater than that of hydrogen chloride, bromide or iodide but less than that of hydrogen fluoride. Consequently, oxygen should displace chlorine, bromine and iodine but not fluorine from their respective hydrides, and this takes place the more readily the greater the difference in the heat of formation.

In fact, we observed (p. 64) that when a flame, or some glowing substance, was brought in contact with a mixture of hydrogen iodide and oxygen, all the iodine was separated in the form of vapor, in accordance with the following equation:

$$2HI + O = H_2O \text{ (vapor)} + 2I \quad . \quad . \quad . \quad (+69.2 \text{ Cal.})$$

Oxygen also liberates bromine from hydrogen bromide at a temperature of about 500° (neither hydrogen bromide nor water suffer dissociation at this temperature). Aqueous vapor is also produced. Hydrogen chloride, however, is only partially decomposed by oxygen even at higher temperatures.

Further, in accordance with this idea, in a mixture of chlorine, hydrogen and oxygen, the hydrogen will first unite with chlorine and if any remain then with oxygen, although the heat of formation of water $(H_2,O) = 57.2$ Cal. is greater than that of hydrogen chloride $(Cl_2,H_2) = 44.0$ Cal. For a more exhaustive study of thermo-chemical relations the student is referred to H. Jahn's Grundsätze der Thermochemie (2 Aufl. Wien, 1892), and also to the works of Ostwald and of Nernst (see pp. 49, 66).

COMPOUNDS OF THE HALOGENS WITH ONE ANOTHER.

These compounds, formed by the union of the halogens with one another, are very unstable, and it may be remarked here, that this is also true of most derivatives obtained from elements which are chemically similar.

When chlorine is conducted over dry iodine, the latter being in excess, iodine monochloride results, and when the chlorine is in excess, iodine trichloride is formed.

Iodine Monochloride—ICl—is a red crystalline mass, fusing at 24.7°, and distilling a little above 100°. Water decomposes it easily, with formation of iodic acid, iodine, and hydrogen chloride. If fused iodine chloride be allowed to solidify slowly at a low temperature (—10°) a modification, melting at +14°, is produced. The latter, however, reverts very readily, with heat evolution, to the higher melting body.

Iodine Trichloride—ICl_3—is formed upon mixing iodic acid with concentrated hydrochloric acid, and by the action of phosphorus pentachloride upon iodic anhydride. It crystallizes in long, yellow needles, and, when heated, suffers decomposition into iodine chloride and chlorine (at ordinary pressure, the dissociation commences at 25°). It dissolves in a little water without alteration; but large quantities cause partial decomposition, with formation of iodic and hydrochloric acids.

Iodine Bromide—IBr—obtained by the direct union of the elements, consists of iodine-like crystals, fusing at about 36°.

Iodine Pentafluoride—IFl_5—is produced by the action of iodine upon silver fluoride, and forms a colorless, strongly fuming liquid.

WEIGHT PROPORTIONS IN THE UNION OF THE ELEMENTS. ATOMIC HYPOTHESIS. CHOICE OF ATOMIC WEIGHTS.

In the preceding pages several different and independent methods have been described for the preparation of each of the halogen hydrides. But it is immaterial which of these may be selected in making any of these compounds, for if the product be carefully purified and then analyzed the hydrogen and the halogen will always be present in a definite, unalterable proportion by weight. The percentage composition of the pure halogen hydrides will be found under all circumstances to be the following:

H	5.05	H	2.77	H	1.25	H	0.79
Fl	94.95	Cl	97.23	Br	98.75	I	99.21
HFl	100.00	HCl	100.00	HBr	100.00	HI	100.00

A regularity exists here, which prevails in *all* chemical compounds. For it is not alone in the halogen hydrides, but without exception *in every chemical combination that the constituents occur in definite unalterable proportions by weight.* This observation ascertained by experiment and based upon facts has been called *the law of definite* or *constant proportions*. From the period in which the French chemist Louis Proust victoriously defended it against the attack of his countryman Claude Louis Berthollet, the great theorist, in a remarkable controversy waged from 1799–1807, down to the present no fact has been observed which contradicts the law.

It will be advisable for later considerations that the quantities of the halogens be calculated from the numbers given above for the percentage composition of the haloid acids, which combine with a definite quantity by weight of hydrogen, the constituent common to these four compounds. For reasons to be discussed later hydrogen is no longer taken as unit, as has been done in the past, and it will be better, therefore, to compare the quantities by weight of the elements with one another, which are capable of uniting with 1.01 parts by weight of hydrogen. In this manner we arrive at the following numbers:

H	1.01	H	1.01	H	1.01	H	1.01
Fl	19.	Cl	35.45	Br	79.96	I	126.85
HFl	20.01	HCl	36.46	HBr	80.97	HI	127.86

This simple recalculation affords a clearer insight into the ratios by weight according to which the halogens unite with hydrogen. We thus discover that 19 parts of fluorine, 35.45 parts of chlorine, 79.96 parts of bromine, and 126.85 parts of iodine, inasmuch as they are capable of uniting with 1 01 parts of hydrogen, are equal or equivalent to one another. These numbers answer not only for the derivatives of the halogens with hydrogen, but we find them in the compounds of the halogens with one another, and in their derivatives with other elements. Thus in iodine monochloride the chlorine and iodine are present in proportions by weight 35.45 : 126.85 and in iodine monobromide the ratio of bromine and iodine is 79.96 : 126.85. If 10 grams of sodium be converted into fluoride, chloride, bromide, and iodide the quantities of the halogens required for this purpose will again be in the ratio of 19 : 35.45 : 79.96 : 126.85. The same occurs if we substitute potassium, calcium, magnesium, zinc, silver, etc., for sodium. Thus 19 parts by weight of fluorine combine with the following weights of the metals: 23.05 parts sodium, 39.15 parts potassium, 32.7 parts zinc, 31.8 parts copper, 100.15 parts mercury,—and 35.45 parts chlorine, 79.96 parts bromine, and 126.85 parts iodine combine with exactly the same quantities by weight of these metals.

Let us take another example. On bringing copper into a solution of a mercuric salt the former dissolves, while mercury separates out; indeed, 31.8 parts of copper displace 100.15 parts of mercury. If zinc be brought into the copper solution thus obtained, it will dissolve, while copper separates—and 32.7 parts of zinc separate 31.8 parts of copper. Furthermore, zinc displaces the hydrogen in acids; from all of them 32.7 parts of zinc separate 1.01 parts of hydrogen. In all these reactions we observe the elements appearing in the same quantities by weight.

There is a net of perfectly definite proportions, by weight, connecting all these bodies with one another, and also the reactions which occur between them. 1.01 parts of hydrogen combine with 35.45 parts of chlorine, and this quantity of the latter with 23.05 parts of sodium, 31.8 parts of copper, 32.7 parts of zinc. 32.7 parts of the latter metal precipitate 31.8 parts of copper and 100.15 parts of mercury, from their salt solutions, and these quantities of the two metals are capable of uniting with the quantities of fluorine, bromine, and iodine which, like the 35.45 parts of chlorine, combine with 23.05 parts of sodium or 1.01 parts of hydrogen, etc. Proceeding in this way with 1.01 parts by weight of hydrogen we obtain a number for each element which may be called its *combining weight*. It will be discovered that the atomic weight of oxygen ($O = 16$) is the basis of all these number ratios. What has been written may be summarized thus: *The elements combine with one another in the ratio of their combining weights.*

A series of very important facts, however, compels us to accord this law a broader meaning. It often transpires that two elements combine with one another not only in one proportion by weight, as in the case of the halogens and hydrogen, but in several ratios. Thus, there are two compounds of chlorine with iodine—the monochloride and the trichloride. The first of these always contains 35.45 parts by weight of chlorine to

126.85 parts by weight of iodine, and the second 3 × 35.45 = 106.35 parts of chlorine to the same quantity of iodine. Two compounds of hydrogen and oxygen are known: water and hydrogen peroxide. In water there are always 8.00 parts by weight of oxygen to 1.01 parts by weight of hydrogen, while in the peroxide to 1.01 parts of hydrogen there are 8.00 × 2 = 16 parts of oxygen. 35.45 parts of chlorine combine not only with 31.8 parts of copper and 100.15 parts of mercury, but also with 63.6 parts of copper and 200.3 parts of mercury. Oxygen forms five distinct compounds with nitrogen with the following proportions by weight, in which 8, the combining weight of oxygen (see above), is made the basis of comparison:

	NITROGEN.	OXYGEN.	
Nitrous Oxide, ...	14.04 parts	8 parts	
Nitric Oxide, ...	14.04 "	16 "	= 2 × 8.00
Nitrous Anhydride, ...	14.04 "	24 "	= 3 × 8.00
Nitrogen Dioxide, ...	14.04 "	32 "	= 4 × 8.00
Nitric Anhydride, ...	14.04 "	40 "	= 5 × 8.00

Proust observed that two elements could combine with each other in different proportions by weight and that in so doing the composition changed by definite increments. The underlying law, however, was first recognized and propounded (evidently as the result of atomic considerations) by John Dalton, and definitely established on a scientific basis through the labors of J. J. Berzelius. It is the *law of multiple proportions: When two elements unite in several proportions, the quantities of the second element combined with definite amounts of the first bear a simple rational ratio to each other.* The law of definite combination by weight can be so expanded that it will at the same time include the law of constant and also that of multiple proportions. Then it would read: *The elements only unite in the ratio of their combining weights or simple rational multiples of the same.*

Compounds, therefore, contain their constituents either in the ratio of their combining weights, or some simple rational multiple of these combining weights—a simple, self-evident, analytical view of the law.

The elements of the doctrine of weight-combinations may be observed and gathered from the investigations of the German chemists—Karl Friedrich Wenzel and Jeremias Benjamin Richter upon the neutralization of bases and acids, and the alternating transposition of salts. Following the example of Richter this division of our science is even yet designated stoichiometry (*τὰ στοιχεῖα*, the constituents; *μέτρον*, measure), and the laws just deduced are the *stoichiometric laws.* It was in this particular direction that Berzelius, from 1808 forward, achieved so much by many hundred accurate analyses which aided very materially in establishing a foundation of irreproachable facts for the preceding doctrine.

[Wenzel: Die Lehre von der Verwandtschaft, Dresden, 1777; Richter: Ueber die neueren Gegenstände der Chemie; besonders im 7, 8, and 9 Stück, 1796–1798. Compare also: Berzelius' Lehrbuch der Chemie, 5 Aufl., Bd. III, 1147; and Versuch, die bestimmten und einfachen Verhältnisse aufzufinden, etc., in Ostwald's: Klassiker der exakten Wissenschaften, Nr. 35.]

The statements thus far made have been free from assumption and have been proved by experiment and analysis; they find mathematical expression in the law of chemical proportions. But now speculation enters. To explain the remarkable regularities in the ratios John Dalton took refuge in the atomic hypothesis—"one of the greatest steps of which chemistry availed itself in advancing to perfection"—Berzelius.

As previously indicated in the introduction (p. 25) Dalton assumed that the elementary atoms preferred uniting in the ratio of 1 : 1; and whenever but one compound of two elements appeared Dalton regarded it as composed of an atom of each of the two elements. If several compounds existed he viewed the first as consisting of A + B, the second of A + 2B, the third of 2A + B, and the fourth of A + 3B (New System of Chemical Philosophy, vol. 1 (1808)). By this assumption the facts, expressed in the stoichiometric laws, meet with an astonishingly simple explanation. If hydrogen chloride contains one atom of hydrogen to one atom of chlorine its composition must always be the same: *law of constant proportions.* If an atom each of hydrogen, sodium, potassium, silver, etc., unite with an atom of fluorine, chlorine, bromine, and iodine to form the corresponding fluoride, chloride, bromide, and iodide, then in all these compounds the fluorine, chlorine, bromine, and iodine must appear in the same constant combination ratios, *i. e.*, the quantities of fluorine, chlorine, bromine, and iodine, which unite with a definite quantity of another element, must always be to one another as their atomic weights: *law of combining weights.* If iodine at one time unites with one atom and again with three atoms of chlorine, the quantities of the latter which iodine in one instance requires to yield the monochloride and at another time the trichloride stand in the proportion of 1 : 3 (Cl : 3Cl): *law of multiple proportions.*

If two elements combine in but one proportion by weight then the resulting compound, on the assumption of Dalton, contains one atom of each element. This at once makes it possible to determine the ratio of the atomic weights of these elements. Thus, in hydrogen chloride there are 97.23 per cent. of chlorine to 2.77 per cent. of hydrogen, and on the assumption of Dalton the compound consists of one atom of hydrogen and one atom of chlorine, then these numbers possess a deeper meaning, for in that case the atomic weights of the two elements will be as 2.77 : 97.23. Similarly, the ratios of the atomic weights of the other elements may be determined and the *relative atomic weights* would result just as soon as some number is selected as the atomic weight for any one element and the proportion numbers are referred to this number. The comparison element should be one which forms analyzable derivatives with most of the other elements. The number selected for its atomic weight is a matter of practicability and of general agreement. These are the reasons which were potent in the choice of oxygen as the standard. Its atomic weight has been placed at 16. Our relative atomic weights, therefore, refer to O = 16. Compare Bericht der Kommission für die Festsetzung der Atomgewichte (Landolt, Ostwald, Seubert), Ber. 31 (1898), 2761.

Hydrogen, the specifically lightest element, was chosen by Dalton as the standard; its atomic weight was taken as unit. The disadvantage in this instance is that hydrogen forms comparable derivatives, allowing of accurate analysis, with few elements. Consequently the ratio of its atomic weight to that of other elements is usually determined with the aid of oxygen. Since, however, the ratio of oxygen to hydrogen cannot be as sharply determined as that of oxygen to the atomic weights of many other elements, errors which are not justifiable creep into the atomic weights by virtue of this recalculation. These reasons led Berzelius, to whom we are indebted for the first accurate atomic weight determinations, to reject the Dalton unit. He chose, with analytical acuteness, oxygen as the standard, setting its atomic weight at 100 (O = 100).

About the middle of the present century a return to the Dalton hydrogen unit occurred. The movement was inaugurated mainly by the French, in order to distinguish new theoretical views at first sight from the older notions held by Berzelius and his students. The standard has met with almost universal adoption from that period down to the present time.

In a recalculation of the atomic weights, conducted by L. Meyer and Carl Seubert (1893) with all previous determinations as basis, the atomic ratio O : H = 15.96 : 1 was assumed as the most probable. Hitherto it has been regarded as the most satisfactory by the majority of chemists and has been adopted in this and other text-books. Since, however, J. Thomsen (1895) and particularly E. W. Morley by a series of most admirable and painstaking experiments have redetermined this ratio, the unsatisfactoriness of the hydrogen unit has become more apparent. All atomic weights determined in ratio to oxygen are affected by the change in this proportion O : H. To avoid similar difficulties in the future—for the ratio O : H cannot be regarded as definitely decided—chemists have taken oxygen as the element of comparison, and in order that the new atomic numbers may be as similar as possible to those previously used, the suggestion of Ostwald that the atomic weight of oxygen be placed at 16 has been followed. The atomic weight of hydrogen will then be H = 1.008, or for all practical purposes H = 1.01. Compare the historical data in the Zeit. f. anorg. Chem. 14 (1897), 250, 256, and also the report of the Atomic Weight Commission to which reference has already been made.

The relative atomic weights, determined in the manner indicated, are, of course, only correct if our assumption as to the number of atoms in union with one another is correct. The chemical analysis of water shows it to consist in one hundred parts of 11.2 parts of hydrogen, and 88.8 parts of oxygen, hence 2.02 parts of hydrogen correspond to 16 parts of oxygen. If, then, water contains one atom of oxygen in union with one atom of hydrogen the atomic weight of hydrogen would be 2.02 (O = 16). It may be possible, however, that water consists of two atoms of hydrogen and one atom of oxygen or of one atom of hydrogen and two atoms of oxygen, etc. In the first case the atomic weight of hydrogen would be 1.01 and in the second 4.04, etc., etc.

Analytical results afford nothing positive for the solution of this difficulty. This was the condition in which the question relating to the magnitude of the atomic weights existed fifty years ago. To establish these correctly, various views were allowed to prevail, none, however, with positive foundation. The question can only be solved upon a basis of special views of the gaseous condition and new facts lying chiefly in the domain of organic chemistry.

Nothing definite is known as to the actual magnitude of the atomic weights. This has thus far been an unimportant matter for purely chemical consideration.

GENERAL PROPERTIES OF GASES. ATOMIC-MOLECULAR THEORY.

Gases, *i. e.*, aeriform bodies, above their critical temperature, possess properties in pronounced degree which are independent of their chemical composition. As regards alterations of pressure and temperature a given volume, for example, one liter, of hydrogen deports itself in the same regular manner as one liter of any other gas under the same conditions. Here chemical composition no longer plays a rôle. Just as soon as a substance passes into the gas condition it acquires the properties expressed by the laws about to be discussed.

The relations between a volume of gas and the pressure under which it exists are expressed, for like temperatures, in a law named after its first discoverer, Boyle (1662), although it often appears under the name of Mariotte (1679). It reads: *the volume occupied by a given mass of gas under different pressures is inversely as the pressure.* If the pressure is trebled the volume will be diminished to one-third; if the pressure falls to one-half, the volume will double, etc. If the gas volumes be represented by v, v' and the pressures by p, p', the law can be algebraically expressed in the equation

$$p : p' = v' : v$$

or

$$p : v = p' : v' = \text{Constant.}$$

That is, the product of the pressure and volume of a given quantity of gas, with constant temperature, is unalterable.

The second law was discovered in 1802, almost simultaneously, by Gay-Lussac and by Dalton. It reads: the volume of any gas increases $\frac{1}{273}$ or 0.003665 of its volume at 0°, for every degree centigrade which its temperature rises under the same pressure. This number, the coefficient of expansion of gases, is ordinarily represented by the letter α. If the volume v_0 of the gas at 0° was equal to 1, then at 1° it is equal to 1.003665, at 273° equal to 2, and universally at t°

$$v_t = v_0 + v_0 \,.\, 0.003665 \,.\, t = v_0 \,(1 + \alpha t).$$

By combining the two laws there results the important equation

$$p\,v = p_0\,v_0\,(1 + \alpha t),$$

indicating the relations between the volume v, which a gas under pressure p occupies at t° and the volume v_0 at 0° under the pressure p_0. We shall return to this law when the measurement of gases and their variation from the Boyle–Gay-Lussac law are considered.

A third law relates to the volume ratios according to which gases combine chemically with one another. These were first investigated by Gay-Lussac, partly in conjunction with A. v. Humboldt. Gay-Lussac announced his observations as follows: The gases combine according to simple volume ratios; the volume of a compound gas bears a simple ratio to the volume of its constituents. In the union of hydrogen and a halogen to form a halogen hydride it was found that one volume of hydrogen and one volume of halogen combine to two volumes of the halogen hydride. Hence, in this instance, the union took place without change of volume; the halogen hydride occupied the space previously occupied by its constituents: an important fact for the chemical atomic theory. It is concluded from this and the previously mentioned facts, according to which hydrogen and halogen unite with one another in the ratio of their combining weights, that the ratio between the weights of equal volumes of these gases, *i. e.*, of their densities, must be the same as that between the combining weights. Each halogen has but one derivative with hydrogen. Hence, according to Dalton, it may be assumed that in the case of the halogens the combining weight and atomic weight are the same. Then their gas density would be proportional to their atomic weights. Here, again, and also in similar deportments of the simple as well as the compound gases, expressed in the law relating to gases, we are forced to the assumption that in equal volumes of different gases there is an equal number of atoms—smallest particles. Dalton and Berzelius both assumed this conception, but soon abandoned it because it did not lead to a definite, well-defined distinction, justified by facts, between elementary and compound gases. Equal volumes of hydrogen and of chlorine unite without any change in volume to hydrogen chloride. If 1000 atoms are present in a given volume of hydrogen, 1000 atoms of chlorine would be required in an equal volume, and by their union there would result 1000 particles of hydrogen chloride, which would occupy, as demonstrated by experiment, the same volume as the chlorine and hydrogen together:

$$\underset{\text{1 vol.}}{1000\,H} + \underset{\text{1 vol.}}{1000\,Cl} = \underset{\text{2 vols.}}{1000\,HCl.}$$

A volume of hydrogen chloride, therefore, would contain only half as many particles as a like volume of the elementary gases—a conclusion which contradicts everything known relative to the constant, physical deportment of the gases (being independent of chemical constitution) with reference to the laws of Boyle and Gay-Lussac.

To solve this contradiction has required almost a half century of chemical investigation. It was especially the advances in the domain of organic chemistry which led to the assumption that the elementary substances as well as the compound did not consist of a mass of free atoms but of an aggregation of atom-groups—of *molecules* (p. 24). This had been advocated (enunciated) by Avogadro (1811), then by Ampère (1814), and subsequently by Dumas (1829), but it was only at the close of the '50's that the theory, after being supported by the Parisian chemist Gerhardt on a purely chemical basis, received general acceptance and favor [Gerhardt, Lehrbuch der organ. Chemie, deutsche Ausgabe, 4 (1857), 598, 627, etc.]. It is, consequently, necessary to distinguish between atom and molecule (*molecula*, mass-particles). It is not the atoms but the molecules which, as a rule, exist in the gases as the smallest constituent particles (exceptions will be discovered later; see also p. 55 on the Dissociation of the Halogens). It is obvious that the smallest particles of a compound body consist of several atoms. By further subdivision such a molecule breaks down into dissimilar constituents: a molecule of hydrogen chloride is resolved into hydrogen and chlorine. Even the elements, when free, consist, as a rule, of molecules, and the latter of several, generally of two, atoms. Hence, the previously deduced rule that in equal volumes of the elementary gases there is contained an equal number of atoms must be changed and amplified somewhat as follows:

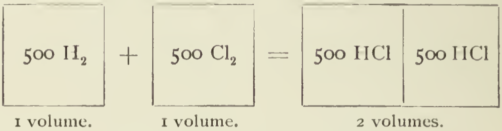
The number of molecules in a unit volume of all gases is the same—like pressure and like temperature being presupposed. While not entirely correct, this law is very frequently designated as the law of Avogadro.

The contradiction between the conclusions deduced from chemistry and from physics now vanishes.

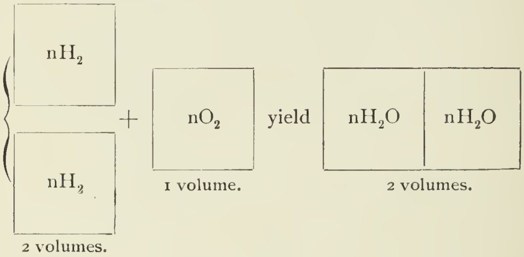
The process of the combination of hydrogen with chlorine (and the other halogens) must be conceived, therefore, to be somewhat like the following: one molecule of hydrogen, containing at least two atoms of hydrogen, acts upon one molecule of chlorine, also composed of at least two atoms of chlorine, and there result two molecules of hydrogen chloride:

$$H_2 + Cl_2 = 2HCl.$$

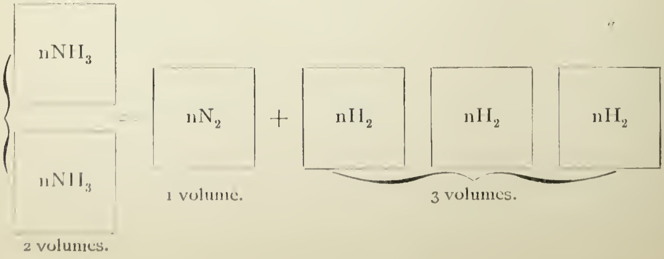
i. e., hydrogen chloride contains just as many molecules in an equal volume as hydrogen and chlorine. This is apparent from the following representation, which attaches itself to the example given on p. 75:



In a similar manner two volumes of hydrogen (containing $2n$ molecules) give with one volume of oxygen (containing n molecules) two volumes of aqueous vapor; consequently, $2n$ molecules of water. In $2n$ molecules of the latter (H_2O) there are contained at least $2n$ atoms of oxygen; therefore, in n molecules of oxygen, $2n$ atoms of oxygen—or *one oxygen molecule consists of at least two atoms* (compare pp. 73, 80).



Let us take another analytical example. Two volumes ($2n$ mol.) of ammonia gas break down, under the influence of the electric spark, into one volume (n mol.) of nitrogen and three volumes of hydrogen (each n mol.). From this it is evident, as in the preceding example, that the nitrogen molecule also is composed of at least two atoms:



In the same way it may be shown that the phosphorus molecule consists of at least four atoms of phosphorus (P_4), etc., etc.

Many other facts corroborate the assumption that the molecules of the elements consist of several atoms, for example, the existence of the allotropic modifications of the elements (compare Ozone), the chemical reactions (compare Hydrogen Peroxide), and the remarkable action of the elements in the moment of their liberation.

We saw (p. 53) that the oxygen separated from water by chlorine acted much more energetically than free oxygen. Other elements, especially hydrogen, behave similarly in the *moment of formation—in statu nascendi*. As viewed by the atomic molecular theory, this may be very easily explained. The free elements (their molecules) are compounds of similar atoms whose chemical affinity has already been partly satisfied. In the moment of their separation from compounds free atoms appear, which, before they combine to molecules, must act more energetically.

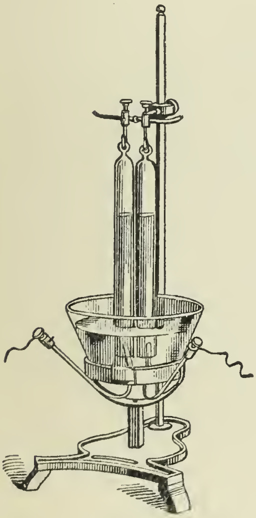


FIG. 37.

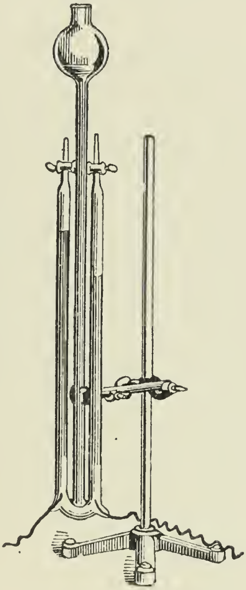


FIG. 38.

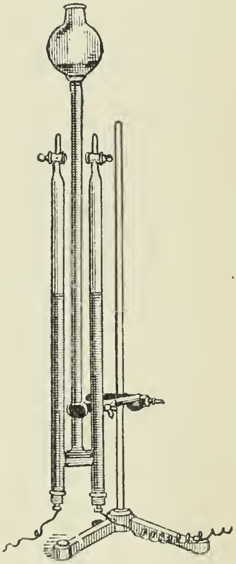


FIG. 39.

The experiments illustrating and confirming what has been said upon the volume relations of the gases will now be considered:

1. The concentrated aqueous solution of hydrochloric acid is decomposed by the action of the galvanic current, and the chlorine and hydrogen collected; these gases separate at opposite poles. The electrolysis may be made in an ordinary voltameter (Fig. 37). Hofmann's apparatus is better adapted to this purpose (Fig. 38 *). Two glass cylinders,

---

* Fig. 38 represents the volume relations of the gases liberated in the electrolysis of water; compare p. 92.

provided at the top with stop-cocks, are connected at the lower end with one another and with a funnel tube ; the latter serves to fill the apparatus with liquid ; and also, by further additions, to press out the gases collected in the tubes. The platinum electrodes are fused into the lower part of both tubes. In another form of Hofmann's apparatus (Fig. 39) the electrodes are introduced by means of caoutchouc stoppers. When the separating gases (in this case chlorine) attack the platinum, carbon electrodes are substituted for the latter.

To electrolyze hydrogen chloride, fill the apparatus with hydrochloric acid, of specific gravity 1.125, to which has been added fifteen times its volume of calcium chloride of 1.36 specific gravity ; close the upper stop-cocks and connect the electrodes with the poles of the battery. Gases separate in both tubes, and in *equal volumes ;* that separated at the positive pole is chlorine ; the other combustible gas is hydrogen. [See Lüpke, Grundzüge der wissensch. Elektrochemie, Berlin, 1899 ; Lothar Meyer, Ber. **27** (1894), 850 ; Haber and Grimberg, Z. f. anorg. Ch. **16** (1898).]

This experiment shows that hydrogen chloride decomposes into equal volumes of chlorine and hydrogen.

2. The production of hydrogen chloride by the union of equal volumes of hydrogen and chlorine is shown in the next experiment.

Fill a cylindrical glass tube, provided with stop-cocks at both ends (Fig. 40), with equal volumes of chlorine and hydrogen. This is most conveniently done by conducting the gaseous mixture obtained by the electrolysis of hydrochloric acid into the dry tube. (The tube should be filled and kept in the dark, as the gases combine in daylight.) When the tube is filled with the mixture, sunlight or magnesium light is directed upon it, when chemical union ensues. On immersing the lower end of the tube into water, and opening the lower stop-cock, the water will rapidly fill the tube, as the hydrogen chloride that was produced dissolves ; all the hydrogen and all the chlorine have disappeared.

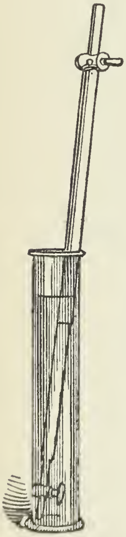


FIG. 40.

3. A modification of this experiment teaches us another important fact which has reference to the ratio of the volume of the hydrogen chloride to the volumes of its constituents. If the tube filled with equal volumes of chlorine and of hydrogen be opened under mercury, after the explosion, no diminution in volume will be detected, although the mixture of chlorine and hydrogen has been changed to hydrogen chloride. It follows from this that a mixture of equal volumes of chlorine and hydrogen affords the same volume of hydrogen chloride, or, as ordinarily expressed, *one volume of chlorine and one volume of hydrogen yield two volumes of hydrogen chloride.*

The following experiment confirms this conclusion : Into a bent tube (Fig. 41), filled with mercury, conduct dry hydrogen chloride, and then introduce in the bend of the upper part a little piece of metallic sodium. On heating the latter with a lamp, the hydrogen chloride is decomposed, the chlorine combines with the sodium to form sodium chloride, while hydrogen is set free. Upon measuring the residual hydrogen it will be found that its volume is exactly the half of the volume of hydrogen chloride originally introduced. In the same manner may be shown the fact that in two volumes of hydrogen bromide and hydrogen iodide there is contained in each one volume of hydrogen. It follows further from the densities of bromine and iodine vapors, that the quantities of these elements in gas form combining with one volume of hydrogen also occupy one volume. Hence, *one volume of hydrogen and one volume of bromine vapor yield two volumes of hydrogen bromide, and one volume of hydrogen and one volume of iodine vapor two volumes of hydrogen iodide.*

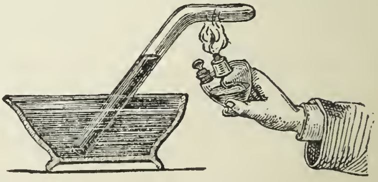


FIG. 41.

All that has been previously stated may be summarized as follows:

1. *All bodies are composed of atoms.*
2. *The atoms unite to form the molecules of the simple and compound bodies.*
3. *Equal volumes of gases contain, at like temperature and under like pressure, an equal number of molecules.*
4. *The gas densities, therefore, bear the same ratio to one another as the molecular weights.*

The gases argon and helium, recently discovered in the atmosphere, are exceptions. They consist of single atoms at the ordinary temperature. This is also true of the halogens at elevated temperatures, and, so far as we know, of metal vapors (mercury, cadmium, zinc).

Heretofore gas density has been referred to the hydrogen atom (H = 1), while the molecular weight was referred to the molecule $H_2 = 2$, so that the density (the specific gravity of the gas) was one-half of the molecular weight. At present, the atomic weight of oxygen (16) being taken as the standard in determining the atomic numbers of the other elements, it appears proper to refer the density to the molecular weight of oxygen, $O_2 = 32$, *when the values for density and molecular weight will coincide.*

The following table contains the atomic and molecular weights of certain metalloids as well as the molecular weights of their hydrogen derivatives. The molecular weights (gas densities) show how much a volume of the respective gas weighs, if an equally large volume of oxygen, under similar external conditions, be placed at 32 (p. 73):

ATOMIC WEIGHTS.	MOLECULAR WEIGHTS OR GAS DENSITIES.
H = 1.01	H_2 = 2.02
Cl = 35.45	Cl_2 = 70.9
Br = 79.96	Br_2 = 159.92
	Br = 79.96 above 1000°
I = 126.85	I_2 = 253.70
	I = 126.85 above 1500°
	HCl = 36.46
	HBr = 80.97
	HI = 127.86
O = 16	O_2 = 32
	H_2O = 18.02
N = 14.~~4~~0	N_2 = 28.08
	NH_3 = 17.07
P = 31.0	P_4 = 124.00
	PH_3 = 34.03

As one liter of oxygen, under normal conditions (p. 44), weighs 1.4291 grams, the weight of one liter (L) of a gas of molecular weight M can be calculated from the equation

$$L = \frac{1.4291 \cdot M}{32} = 0.04466\ M.$$

The density D of the gas, referred to air as unit, follows from the equation

$$D = \frac{M}{28.95}$$

because the density of air is $\frac{32 \cdot 1.293}{1.4291} = 28.95$, referred to $O_2 = 32$.

The numbers deduced from these equations vary somewhat from those obtained by direct observation. This is due to the fact that what has been said is a simple but at the same time not an absolutely correct expression of the deportment of gases. We shall return to this point when the measurement of gases is discussed.

By determining the gas density it is only possible to fix the molecular weight of an element which exists in the gaseous condition. The magnitude of the atomic weight remains uncertain. The chlorine molecule weighs from its gas density and the standard selected 70.9 units, and consists of two atoms (Cl_2), if we suppose that the atomic weight $= 35.45$. Its atomic weight could, however, be only the half (or another submultiple) of 35.45; then its molecule would consist of four chlorine atoms ($Cl_4 = 70.90$ when Cl is made equal to 17.725), and the formula of hydrogen chloride would be HCl_2. As analysis and the vapor density determination of many, especially organic, derivatives show that the smallest quantity of chlorine in a molecule of a gasifiable body must always be expressed by 35.45, we can well accept this number as the atomic weight. That the maximum values thus derived have not been found too high, but correspond to the actual relative atomic weights, follows from the agreement of these numbers with the atomic numbers obtained from the specific heat of the elements. The complete certainty of their correctness we reach by the law of periodicity, which is deduced from these numbers.

These convincing suppositions and conclusions drawn from actual relations, form the atomic molecular doctrine, which is the foundation of the chemistry of to-day. As this doctrine completely explains the quantitative phenomena arising in the action of the chemical elements upon one another, and as it has been repeatedly confirmed by phenomena of a purely physical nature, and has thereby acquired a high degree of probability, it is only proper and correct that it be designated a theory.

OXYGEN GROUP.

In this group are included the elements oxygen, sulphur, selenium, and tellurium. They are perfectly analogous in their chemical deportment. One atom of each of these elements is capable of uniting with two atoms of hydrogen.

1. OXYGEN.

Atom: $O = 16$. Molecule: $O_2 = 32$.

Oxygen (oxygenium) is the most widely distributed element in nature. It is found free in the air; in combination it exists in water. It is an important constituent of most of the mineral and organic substances.

It was discovered, almost simultaneously, by Priestley, in England, 1774, and Scheele, in Sweden, 1775. Lavoisier, in France, 1774–1781, first explained the important rôle attached to oxygen in processes of combustion, of respiration, and of oxidation.

Preparation.—Heat red mercuric oxide, a compound of mercury with oxygen, in a small glass retort; in this way the oxide is decomposed into mercury and gaseous oxygen:

$$HgO = Hg + O.$$

The following method is commonly pursued in the chemical laboratory: Potassium chlorate, a compound of potassium, chlorine and oxygen, is heated in a glass retort (Fig. 42) or flask, and thus decomposed into solid potassium chloride and oxygen:

$$KClO_3 = KCl + 3O.*$$

The evolution of the gas proceeds more regularly and requires a less elevated temperature if the pulverized chlorate be mixed with ferric oxide or manganese peroxide. (A small portion of the oxygen is ozonized; see p. 84). The liberated oxygen is collected over water.

McLeod (Jr. Chem. Soc., 55, 192) explains the mechanism of the action of manganese peroxide on potassium perchlorate, when heated, as follows: First, the peroxide acts on the chlorate producing potassium permanganate, chlorine, and oxygen, $2MnO_2 + 2KClO_3 = K_2Mn_2O_8 + Cl_2 + O_2$. Secondly, the permanganate is decomposed by heat: $K_2Mn_2O_8 = K_2MnO_4 + MnO_2 + O_2$, and in the third stage the change is probably: $K_2MnO_4 + Cl_2 = 2KCl + MnO_2 + O_2$.

Very pure oxygen may also be obtained by heating potassium bichromate with concentrated sulphuric acid:

$$K_2Cr_2O_7 + 5H_2SO_4 = Cr_2(SO_4)_3 + 2KHSO_4 + 4H_2O + 3O.$$

Besides these many other methods may be employed for the preparation of the gas: *e. g.*, the ignition of manganese and barium peroxides; the decomposition of sulphuric acid at a high heat; the boiling of a solution of bleaching lime with a cobalt salt, etc. These methods, applied technically, will be considered more fully later.

A very convenient laboratory method for the preparation of oxygen consists in allowing dilute hydrochloric acid to act upon a mixture of barium peroxide (2 parts) and manganese peroxide (1 part). The gas is evolved at the ordinary temperatures. If the solid ingredients are mixed with gypsum (1 part) and a little water the mass can be moulded into cubes, and the oxygen then be generated (like chlorine) in a Kipp apparatus (Ber. 20 (1887), 1585). Kassner obtains a regular and continuous flow of the gas by pouring water upon a pulverized mixture of 1 part of barium peroxide and 2½ parts of potassium ferricyanide (red prussiate of potash):

$$BaO_2 + K_6Fe_2(CN)_{12} = K_6BaFe_2(CN)_{12} + O_2.$$

Elkan, in Berlin, furnishes oxygen under 100 atmospheres pressure in steel cylinders for trade purposes. The gas is prepared by the method of Boussingault and Brin, by heating barium peroxide to about 700° under reduced pressure:

$$BaO_2 = BaO + O.$$

The resulting barium oxide is reconverted into peroxide at the same temperature but higher pressure by the oxygen of the air. According to Kassner, calcium plumbate may be similarly applied. It breaks down, under conditions which will be considered later, into lead oxide, calcium oxide, and oxygen:

$$Ca_2PbO_4 = PbO + 2CaO + O.$$

---

* The chemical equations used here and previously are only intended to represent the manner of the reaction, and to express the accompanying relative quantities by weight. It should not be forgotten that free atoms do not exist, but that they always occur combined in molecules. Molecularly written the equation would be:

$$2KClO_3 = 2KCl + 3O_2.$$

A method which will probably be of value later is that of Linde, by which nitrogen is first evaporated from liquid air, and the portions passing over subsequently are found to contain 75 per cent. of oxygen.

Properties.—Oxygen is a colorless, odorless, tasteless gas. One liter of oxygen at 0° C., and 760 mm. pressure, weighs 1.4291 grams (15.9 times more than one liter of hydrogen). Its specific volume equals 699.7 c.c. (p. 45). It is only slightly soluble in water; 100 volumes of the latter dissolve 4.1 volumes of the gas at 0°, and 2.9 volumes at 15°. It is more readily dissolved by absolute alcohol (28 volumes in 100 volumes).

The critical temperature of oxygen is —118°, and its critical pressure equals 50 atmospheres (p. 47). Liquid oxygen under a pressure of 1 atmosphere boils at —184°, and under 9 mm. pressure at —225°. Its specific gravity at —118° equals 0.65, at —139° it is 0.87, and 1.124 at —184° (the boiling point at the ordinary pressure). Liquid oxygen has a bright-blue color (Olszewski).

Oxygen combines with all the elements excepting fluorine, helium, and argon. With most of them it unites directly, accompanied by the evolution of light and heat (p. 57). The burning of combustible bodies in the air depends on their union with oxygen, which is present in the same to the amount of 23 per cent. The phenomena of the respiration of animals are also influenced by the contact of the oxygen of the air—hence the earlier designations of oxygen as inflammable air, and vital air. In pure oxygen the phenomena of combustion proceed more energetically than in air. Ignited charcoal or an ignited sliver inflames immediately in the gas, and burns with a bright light. This test serves for the recognition of pure oxygen. Sulphur and phosphorus ignited in the air burn in it with an intense light. Even iron burns in the gas. To execute this experiment, take a steel watch spring, previously ignited, attach a match to the end, ignite the same, and then introduce the spring into a vessel filled with oxygen gas. At once the match inflames and ignites the iron,

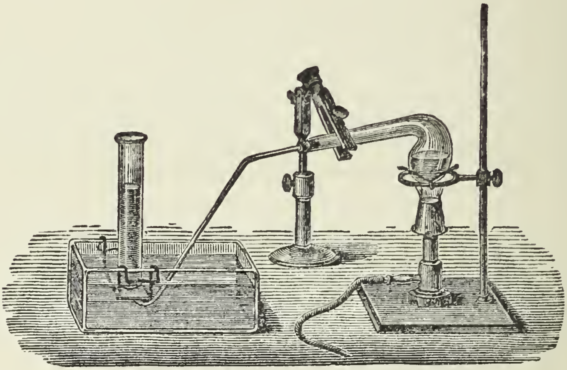


Fig. 42.

which burns with an exceedingly intense light and emits sparks. (To protect the vessel from the fusing globules of iron oxide, cover the bottom with a layer of sand.) Iron will burn in any flame if a current of oxygen be conducted into the same.

Oxygen combines with hydrogen to form water. The union occurs at a red heat, by the electric spark or by the action of platinum sponge (p. 46). Palladium asbestos acts similarly. Of all the combustible gases only hydrogen combines by its influence with oxygen at the ordinary temperature. Hydrogen burns in oxygen with a flame; vice versâ, oxygen must also burn in hydrogen; this may be demonstrated in the same manner as indicated under Hydrogen Chloride (p. 57). A mixture of hydrogen and oxygen detonates violently; most strongly if the proportions are 1 volume of oxygen and 2 volumes of hydrogen; such a mixture is known as oxyhydrogen gas. The explosibility may be shown in a harmless way by the following experiment: Fill a narrow-necked flask of 150–250 c.c. capacity, over water, ⅔ with hydrogen, and ⅓ with oxygen; close the opening with a cork, then wrap the flask in a towel, remove the cork and bring a flame near the opening. A violent explosion ensues, generally with complete breaking of the flask. The temperature of ignition of oxyhydrogen gas is about 650° (V. Meyer and A. Münch, Ber. **26** (1893), III, 2421) (see p. 28).

FIG. 43.

The oxyhydrogen flame is only faintly luminous; it possesses, however, a very high temperature, answering, therefore, for the melting of substances which fuse with great difficulty, *e. g.*, platinum. To get a continuous oxyhydrogen flame, efflux tubes of peculiar construction are employed (Fig. 43); through the outer tube, *W*, hydrogen is brought from a gasometer; oxygen is conveyed through the inner, *S*, and the mixture ignited at *a*. Such a flame impinging on a piece of burnt lime or zircon makes the latter glow and emit an extremely bright light—*Drummond's lime light*, *Zirconium light*.

The union of oxygen with other substances is termed *oxidation*. This term, as well as the name Oxygenium (from *ὀξύς* and *γεννάω*), or acid producer, suggested by Lavoisier, arises from the fact that acids are sometimes formed in oxidation. This the combustion experiments prove. If the vessels, for instance, in which carbon, sulphur, and phosphorus were burned, be shaken with water, the latter will give an acid taste, and redden blue litmus-paper. It was formerly thought that the formation of acids is always conditioned by oxygen. We have, however, already noticed that the haloid acids—hydrochloric, hydrobromic, and hydriodic—contain no oxygen. Some of the elements yield acids by their union with oxygen, or more correctly *oxides*, which form *acids* with water. Most of these are the metalloids. Thus the following corresponding acids are derived from the acid-forming oxides of sulphur and phosphorus:

$$\underset{\text{Sulphur trioxide.}}{SO_3} + H_2O = \underset{\text{Sulphuric acid.}}{H_2SO_4}.$$

$$\underset{\text{Phosphorus pentoxide.}}{P_2O_5} + H_2O = \underset{\text{Metaphosphoric acid.}}{2HPO_3}.$$

With oxygen the metals usually yield oxides, which form *hydroxides* (hydrates) or *bases* with water:

$$\underset{\text{Potassium oxide.}}{K_2O} + H_2O = \underset{\text{Potassium hydroxide.}}{2KOH}.$$

$$\underset{\text{Calcium oxide.}}{CaO} + H_2O = \underset{\text{Calcium hydroxide.}}{Ca\,(OH)_2}.$$

The salts are produced by the alternating action of acids and bases (see p. 61).

Thirdly, there exist the so-called *indifferent oxides*, which yield neither acids nor bases, with water, *e. g.:*

$$\underset{\text{Nitrous oxide.}}{N_2O} \qquad \underset{\text{Nitric oxide.}}{NO} \qquad \underset{\text{Lead peroxide.}}{PbO_2}.$$

Oxidation is not only induced by free oxygen or bodies rich in it, but frequently, also, by the halogens; in the latter case the halogens first decompose the water with the elimination of oxygen, which then oxidizes further (compare p. 53).

The opposite of oxidation, the removal of oxygen, is called *reduction* (p. 64). Hydrogen (*in statu nascendi*), and substances giving it off easily (as hydriodic acid), have a reducing action. Most of the metallic oxides are reduced at a red heat by hydrogen, with the formation of water, *e. g.:*

$$\underset{\text{Copper oxide.}}{CuO} + H_2 = \underset{\text{Copper.}}{Cu} + H_2O.$$

OZONE.

O_3.

Ozone, discovered in 1840, by Schönbein, is, as will be shown later, a peculiar modification of oxygen, characterized by a remarkable odor and great reactivity, therefore it is called *active oxygen.* It is obtained from oxygen in various ways; it is almost always produced when oxygen is liberated, or when it takes part in a reaction; thus, in the decomposition of peroxides by concentrated sulphuric acid, or when they are heated in a current of oxygen to their decomposition-temperature [Brunk, Z. f. anorg. Chem. **10** (1895), 222]; in the electrolysis of water (at the positive pole), in the slow oxidation of moist phosphorus, in the combustion of hydrocarbons, and in the action of the so called silent discharge in an atmosphere of oxygen or air. In none of these instances is all of the oxygen ever converted into ozone; only a small portion—under most favorable conditions 5–6 per cent.—suffers this change.

The following methods serve for the preparation of ozone:

1. Put several pieces of stick phosphorus into a spacious flask, cover them about half with water, and allow them to stand for some hours. Or conduct oxygen over pieces of phosphorus placed in a glass tube and moistened with water. Ozone is also formed abundantly when a potassium bichromate solution is substituted for water. [Leeds, Ann. Chem. 198 (1879), 38.]

2. Pass the silent discharge through air or oxygen. For this purpose we may employ a Siemen's ozone tube (Fig. 44, Geissler form), which consists of two glass tubes *a* and *b* fitting into one another. Each is coated on the inner side with tin foil or gold leaf. The one coating is connected with the positive and the other with the negative pole of an induction apparatus. Oxygen or air circulates between the two tubes in the direction indicated by the arrows.

3. Gradually add barium peroxide in small portions (or potassium permanganate) to cold sulphuric acid:

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O + O.$$

The escaping oxygen is tolerably rich in ozone, and is collected over water.

Ozone possesses a highly penetrating, peculiar odor (hence its name from ὄζειν, to smell), which by prolonged respiration produces bad results. In a thick layer, ozone shows a bluish color. If ozonized air be subjected to powerful pressure (150 atmospheres) at a very low temperature, or if ozonized oxygen be conducted through a small tube cooled to —184° by boiling oxygen, the ozone will condense to a liquid with an indigo-blue color. Liquid ozone, if preserved in a sealed tube, passes into a blue gas, that can be again liquefied by chilling it with boiling ethylene. Ozone is rather stable at the ordinary temperature; and at more elevated temperatures does not revert to ordinary oxygen as rapidly as it was supposed. This was gathered from the experiments of Brunk, according to whom ordinary oxygen is ozonized when it is conducted over manganese peroxide heated to 400°. According to Mailfert's experiments ozone is fifteen times more soluble in water than oxygen. At the ordinary temperature it takes up half its volume of the gas. In solution the ozone gradually reverts to oxygen without formation of hydrogen peroxide. Unlike ordinary oxygen, ozone, especially in a moist state, oxidizes strongly at ordinary temperatures. Phosphorus, sulphur, and arsenic are converted into phosphoric, sulphuric, and arsenic acids; ammonia is changed to nitrous and nitric acids; silver and lead are converted into the corresponding peroxides; therefore paper moistened with a lead salt is colored brown. Iodine is separated at once from potassium iodide by it:

$$2KI + H_2O + O_3 = 2KOH + I_2 + O_2.$$

It also oxidizes all organic substances; therefore the apparatus used in its preparation must not be constructed of caoutchouc. Solutions of dyestuffs, like indigo and litmus, are decolorized. Its ability to turn an alcoholic solution of guaiacum tincture blue is very characteristic of ozone.

For the detection of ozone the ordinary potassium iodide starch-paper (Schönbein) may be used. This is prepared by immersing white tissue-paper in a starch solution mixed with potassium iodide. The iodine which the ozone liberates from the potassium iodide blues the starch-paper. The quantity of ozone may be approximately determined from the rapidity and the intensity of the coloration. Thallous hydroxide is a more reliable reagent for ozone than the potassium iodide starch-paper. Guaiacum tincture and paper saturated with a lead acetate solution may also be used to detect ozone; the first acquires a blue color, the second becomes brown. Other substances also blue potassium iodide starch-paper and guaiacum, *e. g.*, chlorine, bromine, nitrogen dioxide, etc., etc. To distinguish ozone from these, proceed as follows (Houzeau): Take two strips of violet litmus-paper, one of which is saturated with potassium iodide, and expose it to the action of the gas; when ozone is present potassium hydroxide will be formed from the iodide, and color the violet litmus blue. The second paper serves to show the absence of ammonia.

The preceding reactions of ozone are all produced by hydrogen peroxide, although less rapidly. The only test answering for the distinction of very slight quantities of ozone from hydrogen peroxide is the blackening of a bright strip of silver by ozone.

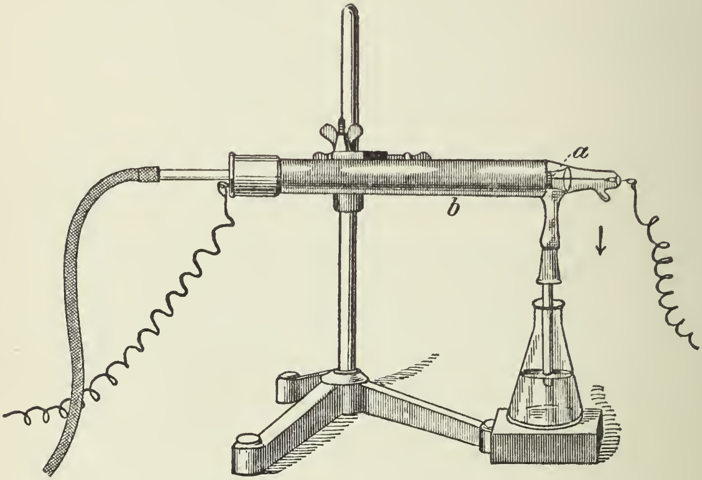


Fig. 44.

Ozone is a variety of oxygen; its molecules consist of three atoms:

$$\underset{\text{3 vols. oxygen.}}{3O_2} \quad \text{yield} \quad \underset{\text{2 vols. ozone.}}{2O_3}.$$

This is proved by the following experiments: In ozonizing oxygen its volume diminishes; upon heating (when ozone is again changed to oxygen), the original volume is reproduced; when ozonized oxygen is brought in contact with oil of turpentine or oil of cinnamon, all the ozone is absorbed and the volume of the gas is diminished. Comparing this diminution, corresponding to the ozone volume, with the expansion which an equal volume of ozonized oxygen suffers after the application of heat, we will find that the first is twice as large as the latter; this indicates that 1 volume of ozone yields 1½ volumes of oxygen (Soret). From this it follows that the specific gravity of ozone must be 1½ times greater than that of ordinary oxygen, and that if the molecule of oxygen consists of two atoms, the molecule of ozone must contain three atoms. This conclusion is confirmed by the specific gravity of ozone derived experimentally from the velocity of diffusion, and has been found to be approximately 48 ($O_2 = 32$), corresponding to the molecular formula O_3 (Graham).

A diminution in the volume of the gas does not occur in the action of ozone upon oxidizable bodies like potassium iodide and mercury, although all the ozone disappears. It would appear from this that, in oxidizing, ozone only acts with one atom of oxygen, while the other two atoms form free oxygen, which occupies the same volume as the ozone:

$$\underset{\text{1 vol.}}{O_3} + 2KI = \underset{\text{1 vol.}}{O_2} + K_2O + I_2.$$

As a consequence of this behavior ozone is also called oxidized oxygen; *i. e.*, free oxygen (O_2), which has combined with an additional oxygen atom.

Thermo-chemical Deportment.—Compared with ordinary oxygen, ozone is an endothermic compound. Heat is absorbed in its formation from oxygen:

$$(O_2,O) + 36.2 \text{ Cal.} = O_3.$$

This explains why ozone is produced with so much difficulty, and why the addition of considerable energy is necessary. This may be applied directly in the form of heat or electricity (electric sparks, silent electric discharge), or it may be withdrawn from the heat of formation of other exothermic compounds which are produced at the same time, *e. g.*, the formation of ozone by the oxidation of phosphorus to phosphorous acid.

Being an endothermic derivative, we readily perceive why ozone is so unstable, and why it changes so readily to ordinary oxygen. When this occurs the oxygen acts as if in the moment of formation ($O_3 = O_2 + O$; see p. 53), and this explains why ozone acts more powerfully than ordinary oxygen. And to this must be added that in oxidations performed by ozone there are 36.2 Cal. more set free than in oxidations with ordinary oxygen.

We observe, therefore, that the elementary substance oxygen occurs in free condition in two different forms—*allotropic modifications*—ordinary oxygen (O_2) and ozone (O_3). We shall learn later that very frequently substances of the same elementary composition possess different physical and chemical properties; such bodies are called *isomerides* and the phenomenon *isomerism* (ἴσος, like; μέρος, part). The isomerism of the elements was called *allotropy* (ἀλλότροπος, differently formed) by Berzelius. It is accounted for (as in the case of oxygen and sulphur) by the different number of atoms in the molecule. Alterations in the molecular energy relations are obviously of great importance. The allotropy of oxygen confirms the conclusion drawn from the gas densities, that the molecules of the elements are composed of atoms.

We have already seen that ozone is absorbed not only by turpentine and cinnamon oil, but also by other ethereal oils. These bodies are, however, very slowly oxidized; the oxygen is contained in them in a peculiar condition. In this form it acts upon some bodies like free ozone; in other instances, the oxidizing action is rendered possible only by peculiar substances which carry the oxygen. Spongy platinum, ferrous sulphate, and the blood-corpuscles are examples of this class. Thus, old turpentine oil, containing absorbed ozone, only acts on paper saturated with starch-paste and potassium iodide, when a few drops of a ferrous sulphate solution have been added to it.

Since ozone is formed when electricity acts upon air, and, indeed, probably, in all oxidation and combustion processes,—and, further, potassium iodide starch-paper is blued when exposed to the air,—it was believed that ozone was a constant constituent of atmospheric air (1–10 milligrams in 100 liters of air); according to recent investigations it is, however, probable that the imagined ozone reactions are frequently produced by hydrogen peroxide, which is very similar in reaction to ozone (p. 103), and is almost constantly in the air (Schöne). [Ber. **13** (1880), 1503; Engler and his co-workers, Ber. **30** (1897), 1669; **31** (1898), 3046.]

Antozone, which was regarded as a third peculiar modification of oxygen, has been proved in some cases to be hydrogen peroxide and in others to be oxygen *in statu nascendi.*

Oxygen is taken up at the ordinary temperature by comparatively few bodies. The alkali metals, finely divided metals, compounds of sulphurous acid, phosphorus, certain organic derivatives, etc., are such "auto-oxidizable" bodies. In their spontaneous oxidation the very remarkable phenomenon has been noticed that other substances, present at the same time and in themselves not oxidizable, are also oxidized. It was therefore said that oxygen was rendered active by the "auto-oxidizable" substances. More recent experiments have proved that the oxidation was occasioned by intermediate products rich in oxygen (peroxides) which readily parted with their oxygen and acted as oxygen carriers. [See Engler and Wild, etc.]

COMPOUNDS OF OXYGEN WITH HYDROGEN.

1. WATER.

Molecule: $H_2O = 18.02$.

Water, the product of the union of hydrogen and oxygen, is produced in many chemical processes, *e. g.*, in the formation of salts from bases and acids (p. 61). Cavendish was the first (1781) to produce water synthetically by the combustion of hydrogen in oxygen. Lavoisier a little later showed by analysis that water contained hydrogen and oxygen (p. 40). The first determination, although far from accurate, of the quantitative composition of water also originated with Lavoisier (1783). The weight ratio of hydrogen and oxygen in it was first determined more correctly by Berzelius and Dulong (1820). Gay-Lussac conjointly with Humboldt (1805) had shown that water was produced by the union of two volumes of hydrogen with one volume of oxygen (p. 74).

Physical Properties.—It is obtained chemically pure by the distillation of naturally occurring water, which always contains other matter dissolved in it. It appears in all three states of aggregation: in the liquid, gaseous (steam), and solid (ice, snow). In a thin layer water is colorless, while it is blue in layers of greater thickness. When water is cooled it contracts and attains its greatest density at +3.98° C. The weight of a cubic centimeter at +4° is taken as the unit of weight (= 1 gram). By further cooling the water expands—the opposite of most other bodies; its volume becomes greater, while the specific gravity decreases.

The following table gives the volume and specific gravity of water for different temperatures referred to water at 4° (see the investigations of Thiesen, Scheel and Diesselhorn, Zeit. f. Instrumentenkunde, **17** (1897), 332):

TEMPERATURE.	SPECIFIC VOLUME.	SPECIFIC GRAVITY.
0°	1.0001324	0.9998676
2°	1.0000320	0.9999680
4°	1.0000000	1.0000000
6°	1.0000320	0.9999680
8°	1.0001241	0.9998759
10°	1.0002730	0.9997271
12°	1.0004756	0.9995246
14°	1.0007292	0.9992713
16°	1.0010314	0.9989697
18°	1.0012000	0.9986220
20°	1.0017728	0.9982303
22°	1.0022083	0.9977966
26°	1.0032006	0.9968097
36°	1.0063297	0.9937101
38°	1.0070584	0.9929911
50°	1.01200	0.98813
100°	1.04327	0.95863

By cooling, water solidifies to ice. The melting point of ice is taken as the zero of the centigrade and Réaumur's thermometric scales. The solidification-temperature of water cannot be used for this purpose, because water at rest can be chilled considerably below 0° without freezing. The freezing point of ice, however, like all other solid bodies, is constant at a definite pressure. As the latter rises the melting point of ice falls. At a pressure of 1000 atmospheres ice melts at —7° (Lord Kelvin). Most other substances, unlike ice, melt with an increase in volume; in their case increase in pressure occasions a rise in the melting point (Bunsen).

In the conversion of water into ice, a considerable expansion occurs: 100 volumes of water at 0° yield 109 volumes of ice at 0°; the specific gravity of the latter is, therefore, 0.9173, referred to water at 4°. This is why ice floats in water. Ice crystallizes in rhombohedral forms of the hexagonal system as may be distinctly observed in snowflakes.

Different bodies require different quantities of heat to bring them to the same temperature. The heat capacity of water is greater than that of all other liquid or solid bodies. It is customary to take the quantity of heat necessary to raise one part by weight of water from 15° to 16° C., as the unit of heat, or calorie (see p. 66). In the passage of a liquid to the solid state heat is always set free, while, on the other hand, in the fusion of the solid heat is absorbed. The *latent* heat of fusion of 1 kilogram of ice equals 79 calories; this means that, for the melting of the ice, a quantity of heat is required which is capable of raising 79 kilograms of water from 15° to 16° (p. 92).

Water boils upon the application of heat, and is converted into *steam*. The boiling temperature, like that of all other liquids, depends on the pressure; it is also influenced by the substances dissolved in it, although the temperature of the vapors is constant (at a given pressure). The temperature of the steam escaping from water at the ordinary pressure of 760 mm. (45° latitude; sea-level) is 100° (= 80° Réaumur). At 680 mm. barometric pressure water boils at 96.9°, and at 800 mm. at 101.4°.

One volume of water at 100° C. yields 1696 volumes of vapor of the same temperature. The specific gravity of steam equals 18.02 ($O_2 = 32$) or $\frac{18.02}{28.95} = 0.622$ (air = 1); see p. 79. One liter of aqueous vapor weighs 0.590 gram at 100° under normal pressure.

The critical temperature of water (or its absolute boiling temperature, p. 48) is +370°, its critical volume 2.33, and its critical pressure 195.5 atmospheres, *i. e.*, at 370° the tension of its vapor equals 195.5 atmospheres, and above this temperature it can no longer exist as a liquid, but only as a gas.

The vaporization of water, and of other liquids, occurs not only at the boiling point, but also at lower temperatures. The tension of the vapor is measured by the height of the column of mercury which holds it *in equilibrio*.

The following table gives the tension of aqueous vapor for various temperatures (expressed in mercury levels at 0°, 45° latitude, and sea-level):

TEMPERATURE.	TENSION.	TEMPERATURE.	TENSION.
—20° C.	0.93 mm.	20° C.	17.4 mm.
—10° C.	2.15 mm.	40° C.	54.9 mm.
0° C.	4.6 mm.	60° C.	148.9 mm.
+10° C.	9.1 mm.	80° C.	355.4 mm.
+15° C.	12.7 mm.	100° C.	760.0 mm.

Moist gases, therefore, occupy a larger volume than those which are dry. (See Air: measurement of gases).

The latent heat of the evaporation of a kilogram of water equals 536.4 heat units at 100° C.; *i. e.*, for the conversion of one kilogram of water at 100° C. into vapor of the same temperature a quantity of heat will be absorbed capable of raising 536.4 parts of water from 15° to 16°.

In consequence of the evaporation of water, the gases separating from an aqueous solution are always moist. To dry the same, conduct them over substances which will take up the moisture, *e. g.*, calcium chloride, stick potash, sulphuric acid, phosphoric anhydride (compare p. 42). Many solids abstract moisture from the air without chemically uniting with it; to dry these let them stand in an enclosed space over sulphuric acid, calcium chloride, or phosphorus pentoxide (desiccators).

Natural Waters.—As water dissolves many solid, liquid, and gaseous compounds, all naturally occurring waters contain foreign admixtures. The purest natural water is rain- or snow-water; it contains about 3 per cent. by volume of gases (oxygen, nitrogen, argon, and carbon dioxide), and traces of solids (the ammonium salts of nitrous and nitric acids). If water that has been standing exposed to the air be heated, the dissolved gases escape in bubbles.

River and spring waters contain solid constituents in widely varying amounts. Water having much lime and gypsum present in it is ordinarily known as *hard*, in distinction from *soft* water, which contains less lime (see Calcium Carbonate). On boiling lime-waters, most of the impurity deposits out. Spring water generally contains in addition larger quantities of carbon dioxide, which impart a refreshing and enlivening taste to it. Spring waters holding considerable quantities of solid constituents, or exhibiting special healing properties, are called *mineral waters.* These are distinguished as saline waters (containing sodium chloride), magnesian waters, sulphur waters (hydrogen sulphide), acidulated waters (saturated with carbon dioxide), chalybeate waters (containing iron), and others.

Sea-water contains 3.5 per cent. of salts, chiefly sodium chloride (2.7 per cent.).

To purify the natural waters they are filtered (for the removal of mechanical admixtures) and, for chemical and pharmaceutical purposes, distilled (*distilled water*) in apparatus of varying form.

Chemical Properties of Water.—Water is a neutral substance, *i. e.*, it possesses neither acid nor basic properties. As we have already observed (p. 61), it forms bases with basic oxides and acids with acid-forming oxides.

Despite the fact that the affinity of hydrogen for oxygen is may great, water may be decomposed by many substances. At ordinary temperatures, metals like potassium, sodium and calcium decompose it, with liberation of hydrogen:

$$2H_2O + K_2 = 2KOH + H_2.$$

Other metals do not decompose it, except at elevated temperatures. Steam conducted over ignited iron gives its oxygen to the latter, forming ferroso-ferric oxide, while hydrogen is set free (pp. 40, 94):

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

This is a *reversible reaction.* Many of these oxides (even sodium oxide, according to Beketoff) are again reduced by hydrogen at more elevated temperatures:

$$Fe_3O_4 + 4H_2 = Fe_3 + 4H_2O.$$

(See pp. 52, 68, 95.)

Chlorine decomposes water in the sunlight; the decomposition is more rapid when the vapors are conducted through heated tubes (p. 52):

$$2H_2O + 2Cl_2 = 4HCl + O_2.$$

Many chemical reactions are only completed in the presence of moisture. Thus, the metals are only oxidized at the ordinary temperature when both oxygen and moisture are present. Iron does not rust in perfectly dry air. Absolutely dry oxygen does not act upon the substances which it ordinarily attacks with great energy. Phosphorus, carbon and carbon monoxide do not burn, or at least but feebly, in perfectly dry oxygen. Dry hydrogen chloride does not turn blue litmus red, etc. [Dixon, Ber. **19** (1886), Ref. 157; Baker, *ibid.* **18** (1885), Ref. 426; Lothar Meyer, Ber. **19** (1886), 1099; R. Otto, Ber. **26** (1893), II, 2050; Hughes, *ibid.* IV, 863; Veley, Ber. **29** (1896), I, 577; also Gutmann, Ann. Chem. **299** (1898), 267; see also p. 101.]

Electrolysis of Water.—The electric current, acting upon water acidulated with sulphuric acid, decomposes it apparently directly into its elements. Hydrogen collects at the negative pole—the *kathode,* while oxygen appears at the positive pole—the *anode.** The volume of the hydrogen is nearly twice that of the oxygen (pp. 76, 98).

The electrolytic decomposition of water is more complex than is ordinarily supposed, as perfectly pure water is not capable of conducting the current, and is consequently not decomposed by it. It is rather the added sulphuric acid which suffers the decomposition and by means of the water is always reformed (compare the Electrolysis of Salts). Hydrogen and oxygen are merely the end-products of this change. In addition to oxygen, about one per cent. of ozone is produced; further, sulphur heptoxide (persulphuric acid) and hydrogen peroxide are formed at the anode. Some hydrogen peroxide is produced at the negative pole (the kathode) as the result of the union of nascent hydrogen with the dissolved oxygen (p. 101).

Thermo-chemical Deportment.—Water is formed from its elements with the liberation of much heat. 57.2 Cal. are disengaged in the union of 2 grams of hydrogen with 16 grams of oxygen to produce aqueous vapor of 100° (H_2, O—vapor). In the condensation of the steam to water of 100° 9.63 Cal. are liberated ($= 18 \times 0.536$); this is the latent heat of evaporation (see p. 89). And again, in the cooling of the water through every 1° C., $\frac{18}{1000}$ Cal. more escape; consequently in cooling from 100° to 16° there would be a liberation of $84 \cdot \frac{18}{1000} = 1.5$ Cal. (see p 66). So that in the production of the molecular weight (18 grams) of water of 16° temperature from its elements there is a total disengagement of 68.3 large calories:

$$(H_2, O\text{ — vapor}) = 57.2\text{ Cal.} \quad (H_2, O\text{ — liquid}) = 68.3\text{ Cal.}$$

The decomposition of water at the ordinary temperature by a metal only takes place if the heat of formation of the oxide is greater than that of the water. Sixteen grams of oxygen in their union with hydrogen liberate 68.3 Cal., with sodium 100 Cal., and with copper but 38 Cal. The decomposition of water by sodium is an exothermic reaction, while that by copper is endothermic (see p. 94).

---

* Faraday introduced the following terms, which have been universally adopted: The metal wires or plates by which the current enters and passes from electrolytes are called the electrodes (*ὁδός*, way); the electrode by which the current enters is the *anode* and the other through which the positive electricity has its exit and by which the negative electricity enters is the *kathode.* That part of the electrolyte passing to the anode where it is separated or deposited is the *anion* (that which migrates upward—opposite to the current of positive electricity) while the portion going to the kathode and separating there is the *kation* (migrating downwards—with the current of positive electricity). Both are called *ions* (*ἰόντα*, wandering, migrating). As a rule the kations in a compound are replaceable by hydrogen; the anions are simple or *compound halogenides* (Cl, SO_4) (compare the Electrolysis of Salts and Electrolytic Dissociation).

Dissociation of Water.—Water, like other chemical compounds, is broken down into its elements by heat. This was first observed upon pouring molten platinum into water, when bubbles of oxyhydrogen gas appeared (Grove). This decomposition of water was first ascribed to a catalytic action of the platinum. Sainté-Claire Deville was the first to carefully investigate and explain the decomposition phenomena induced by heat, thus disclosing one of the most important chapters of theoretical chemistry. He proved that a decomposition (dissociation) like the preceding did not take place suddenly, but gradually; that it advanced regularly with increasing temperature, and was limited by an opposing combination-tendency on the part of the components. The temperature at which the decomposition is half finished is usually designated as the temperature of decomposition.

Deville illustrated the decomposition of water by the following experiment: Pass aqueous vapor through a porous clay tube, *a*, cemented into a wider non-permeable porcelain tube heated to a white heat in an oven (Fig. 45).* The water suffers partial decomposition, the lighter hydrogen, which passes through the inner tube into the porcelain tube more rapidly than the oxygen, escapes through the gas tube *b*. The oxygen escapes mainly through the inner tube at *a*. A part of the same diffuses simultaneously with the hydrogen and reunites with the latter. To avoid this, conduct a stream of carbon dioxide through the wider porcelain tube; this will carry out the hydrogen with it. The carbon dioxide will be absorbed by the alkali solution in the collecting vessel, and oxyhydrogen gas be found in the cylinder. The decomposition of the water commences at about 1000°, and is half finished at about 2500°. The quantity of gas liberated in equal periods rises successively with the temperature.

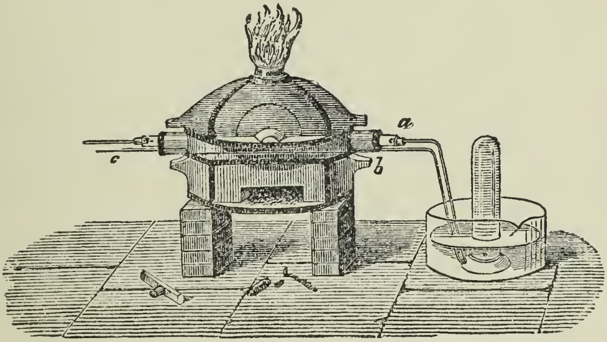


Fig. 45.

Many other compounds, as carbon dioxide, hydrogen chloride, iodine (p. 55), ammonium chloride, phosphorus pentachloride, etc., are simi-

---

* A tube of platinum may be well substituted for the porous clay tube; at a red heat it permits the passage of hydrogen, but not that of oxygen (p. 45).

larly dissociated by heat. These are all exothermic compounds, absorbing energy in their decomposition, and are therefore decomposed but gradually, depending upon the amount of energy imparted to them. In these instances heat opposes the affinity of the various components, so that if the temperature be lowered there will occur a partial reunion of the same. The splitting up of the endothermic compounds is entirely different, *e. g.*, that of potassium chlorate, $KClO_3$, into potassium chloride and oxygen, of ammonium nitrite, NH_4NO_2, into water and nitrogen, of nitrogen chloride into chlorine and nitrogen, etc. Heat is set free in the decomposition of these compounds. Any added or external heat only incites or brings on the decomposition and overcomes the chemical affinity. Under some conditions there are accompanying explosions; there is no reunion of the components on lowering the temperature.

The explanation of the *dissociation* phenomena is found in the kinetic theory of gases (*κίνησις*, motion). According to it the heat-motion of the molecules of a gas is motion in direct lines, progressive and with uniform velocity. As the temperature rises the velocity of this motion increases. Its energy for the molecules of different gases at any given temperature is the same. Heavy molecules move correspondingly slower than the light molecules. The atoms, too, forming the molecule, have their own peculiar motions, which become more energetic with the rise in temperature. By the peculiar motions of the atoms—in which the center of gravity of the molecule is not concerned—the internal arrangement of the molecule is affected; it also opposes the action of affinity. Therefore, just as soon as, by augmented temperature, the centrifugally active energy of atomic motion equals or exceeds the affinity, the breaking down of the molecule takes place. Further, as a consequence of irregular collision, the molecules do not all possess the same velocity at a given temperature; some move more rapidly, others slower, than the main portion; the former are warmer than the latter. Only the sum of the existing forces of all the molecules is a constant quantity at every temperature.

The molecules first decomposed are those moving more rapidly and having a temperature beyond the average temperature. Their number increases with the temperature. Hence, it follows that dissociation also increases with rise of temperature. Compare in this connection W. Nernst and A. Schönflies, Einführung in die math. Behandlung der Naturwissenschaften, 2 Aufl. (1898).

The dissociation of solids, which when heated develop gaseous ingredients, is very instructive and remarkable—for example, the decomposition of calcium carbonate, $CaCO_3$, into calcium oxide and carbon dioxide, of sodium and potassium hydrides (K_4H_2) into their elements, etc. These indicate that the dissociation is not only dependent upon the temperature but also upon external pressure, and that for every temperature there is a corresponding definite tension of dissociation—a pressure below which the decomposition will not occur. For further particulars on this point see Potassium Hydride and Calcium Carbonate.

Dissociation, *i. e.*, the partial decomposition increasing with the temperature, explains many chemical processes and phenomena. Thus it accounts for the abnormal vapor densities, which apparently contradicted the law of the equal number of molecules being present in equal volumes of gases (p. 79); all variations from it are always due to the breaking down of more complex molecules (see Sulphur, p. 106). The observed vapor density affords a clue to the magnitude of the dissociation. The mass action in reversible (inverse) chemical reactions is afforded a simple explanation by dissociation. We have already said that iron raised to a red heat decomposed water with the separation of hydrogen and the production of ferrous-ferric oxide:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

On conducting hydrogen over ignited iron oxides the opposite process occurs; the oxygen compound of the iron is reduced and water and iron are formed:

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O.$$

In the first instance the excess of water acts. Some of its molecules are dissociated; oxygen combines with iron, while the liberated hydrogen is carried away by the excess of steam. In the second case, we can suppose that some of the hydrogen molecules are dissociated, the free hydrogen atoms withdraw oxygen from the iron oxide and form water with it, which is removed by the excess of hydrogen, and thus prevented from acting on the reduced iron.

If, however, iron and steam be heated in an enclosed space for every temperature above 150°, where action begins, there will occur a state of equilibrium: ferrous-ferric oxide, iron, water, and hydrogen will be present together in a ratio which does not alter for any definite temperature, *i. e.*, in a definite period of time as much iron will be produced from the ferrous-ferric oxide by the hydrogen as is oxidized by the water to ferrous-ferric oxide. This may be expressed thus:

$$Fe_3O_4 + 4H_2 \rightleftarrows 3\ Fe + 4H_2O.$$

(See pp. 52, 68, 91.)

Similarly, hydrogen chloride is decomposed at a red heat by oxygen with the formation of steam and chlorine gas, while in turn steam and chlorine gas are transposed into hydrogen chloride and oxygen. As hydrogen chloride is more stable than water and only dissociated at high temperatures, its formation is the predominating process at a red heat. Here, however, in the course of time, a state of equilibrium appears for every given temperature and pressure.

The investigation of the dependence of this state of equilibrium upon temperature, pressure, duration of action, the quantities, concentration, and solubility-proportions of the reacting substances, has become of the greatest importance for theoretical chemistry, for the reason that here for the first time chemical phenomena are capable of a mathematical treatment. The fundamental investigations, both theoretical and experimental, made upon the law of mass-action, which will not be entered upon here, are due to the Norwegians C. M. Guldberg and P. Waage [Études sur les affinités chimiques, Progr. de l'Université Christiania, 1867. See also Jr. prakt. Ch. [2] 19 (1879), 69]. For study use the works, referred to on p. 49, by Lothar Meyer; also the Theoretical Chemistry by W. Nernst, 2 Aufl., 1898.

THE QUANTITATIVE COMPOSITION OF WATER.

The weight and volume relations by which hydrogen and oxygen combine to form water constitute the most important basis for the determination of the ratio of the atomic weights of these two elements to each other. To determine this ratio with such accuracy that no question can longer exist has been the purpose of innumerable investigations since the time of Dalton. Numerous difficulties had to be surmounted. They were found particularly when seeking to obtain the gases perfectly dry, in weighing them, in measuring them, and in endeavoring to combine them. The judgment, care, and untiring patience requisite for the solution of this apparently simple problem may be gathered from the magnificent researches, already referred to, of the American Edward W. Morley (pp. 44, 73).

The composition of water has been chiefly determined by its synthesis which can be followed quantitatively in its details, as both oxygen and hydrogen, as well as the water produced from them, are weighed. The hydrogen is liberated either by the electrolysis of dilute sulphuric acid or sodium hydroxide (Thomsen, p. 42), and according to Keiser, is best weighed as palladium hydride (p. 46). The oxygen is obtained by heating potassium chlorate. Chemists have frequently been satisfied, instead of weighing the three bodies, hydrogen, oxygen, and water, to merely weigh two of them. This was true of Berzelius and Dulong (1819), Erdmann and Marchand (1842), and Dumas (1843), who proceeded according to a method which has become classic: hydrogen was conducted over ignited copper oxide, which was reduced to metallic copper, with the formation of water:

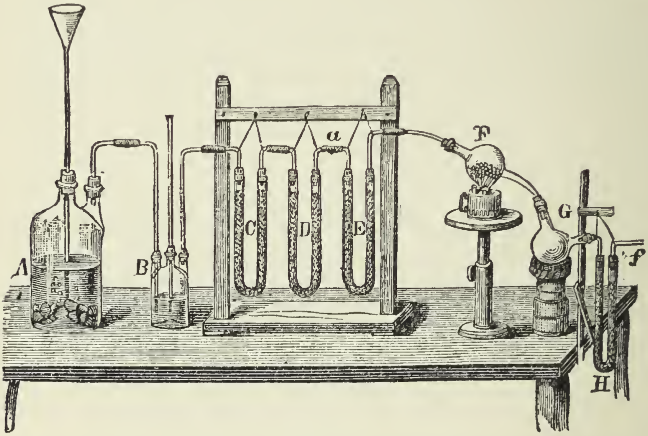


FIG. 46.

$$\underset{\text{Cupric oxide.}}{CuO} + H_2 = \underset{\text{Copper.}}{Cu} + H_2O.$$

Heat a weighed portion of cupric oxide (containing a definite amount of oxygen) in a stream of pure, dry hydrogen, and weigh the quantity of water obtained. The operation can be executed in the apparatus represented in Fig. 46. It was employed by Dumas. The hydrogen generated in the flask *A* is washed in *B*, and then dried in the tubes *C*, *D*, and *E*, which contain substances that will absorb water. The bulb tube *F*, of difficultly fusible glass, contains a weighed amount of cupric oxide, and is heated with a lamp. The water which forms collects in the bulb *G*, and is completely absorbed in the tube *H*. Hydrogen is led over the cupric oxide until it is reduced to red metallic copper, then allowed to cool, when *F* is weighed alone and *G* and *H* together. The loss in weight of *F* expresses the quantity of oxygen which has combined with hydrogen to produce water. The increase in weight of *G* and *H* gives the quantity of water that was formed. The difference shows the amount of hydrogen in water.

Cooke and Richards modified this method in that they conducted a weighed amount of hydrogen, by means of a dry air current, over the ignited copper oxide, and then determined the weight of the water which resulted.

The composition of water by weight can also be ascertained from the ratio of the specific gravities of the two gases and the volume ratio according to which they combine. The most recent researches (Scott, Leduc, Morley) indicate that 2.0027 volumes of hydrogen unite with 1 volume of oxygen to form water. As one liter of oxygen weighs 1.4291 gram and one liter of hydrogen 0.08988 gram, their weight ratio in water would be

$$1.4291 : 2.0027 \,.\, 0.08988 = 16 : 2.0153.$$

Thus we ascertain that in 100 parts of water, by weight, there are

11.2	parts Hydrogen
88.8	" Oxygen
100.0	" Water.

Ostwald in his Lehrbuch der allgemeinen Chemie, 2 Aufl. (1891), 1, 43, gives a review of the history of these important investigations. See also the researches of Morley and of Thomsen (p. 44).

THE MOLECULAR FORMULA OF WATER. ATOMIC WEIGHTS OF HYDROGEN AND OXYGEN.

The molecular weight of water according to Avogadro's law is 18.02 and that of hydrogen is 2.02 if the molecular weight of oxygen be placed at 32. As to the number of atoms combined to a molecule we can conclude from what has been previously said that the molecules of hydrogen, oxygen, chlorine and hydrogen chloride contain at least two atoms each (p. 75). The facts about to be presented make it probable that these molecules do not consist of more than two atoms and that the molecular formula H_2O represents water (p. 73).

One volume of aqueous vapor contains only one-half as much oxygen as an equal volume of oxygen gas, and in an equal volume of any gaseous oxygen compound less oxygen has never been observed. Hence it may fairly be concluded that there is only one atom of oxygen present in the molecule of water, and that the oxygen molecule itself consists of two atoms.

Again, one volume of aqueous vapor contains just as much hydrogen as an equal volume of hydrogen gas, and twice as much as hydrogen chloride gas. Since, therefore, in equal volumes of other gaseous bodies less hydrogen and less chlorine, than in hydrogen chloride, have never been observed, it may be assumed that the molecule of hydrogen chloride contains one atom each of hydrogen and chlorine, and further that the hydrogen molecule consists of two atoms of hydrogen, the water molecule of one atom of oxygen and two atoms of hydrogen. In this manner we arrive at the molecular and atomic weights given on p. 79; whereby the atomic weight of hydrogen 1.008 is reduced to 1.01.

It seems practicable, for considerations like those given, to introduce several new terms. As the specific volume Vs of a gas we have designated that volume which 1 gram of the gas would occupy under normal conditions (p. 45). The quantity of a substance expressed by the molecular weight in grams should be termed the *gram-molecule* or the *mol.* One mol of oxygen would then under normal conditions be 32 grams. The volume Vm, which would be occupied by 1 mol of a gas of the molecular weight M under normal conditions—the *molecular volume*—would be the specific volume multiplied by the molecular weight:

$$Vm = Vs\,.\,M = 22.4 \text{ liters.}$$

The mol-volume is the same for all gases: a new expression for the so-called Avogadro law. It equals 22.4 liters; *i. e.*, 2.02 grams of hydrogen (H_2), 70.9 grams of chlorine (Cl_2), 36.46 grams of hydrogen chloride (HCl), 32 grams of oxygen (O_2), 18.02 grams of aqueous vapor occupy under normal conditions a volume of 22.4 liters. This is only approximately correct because of the deviations of gases from the requirements of their laws. What has been said in the preceding lines may be expressed thus: Since in 22.4 liters of a homogeneous gaseous compound never less than 1.01 grams of hydrogen, 35.45 grams of chlorine, 16 grams of oxygen, etc., have been discovered, it may be concluded that these express their atomic values.

After having thus derived the molecular formula of water, and the atomic weights of oxygen and of hydrogen, we deduce the following conclusions:

1. Sixteen parts by weight of oxygen occupy the same volume as 1.01 parts by weight of hydrogen; since 16 parts of the former unite with 2.02 parts of the latter in the production of water, one volume of oxygen must combine with two volumes of hydrogen.

2. In equal volumes we have an equal number of molecules; *n* molecules of oxygen (O_2) unite therefore with 2*n* molecules of hydrogen (H_2); the same yield 2*n* molecules of water; consequently two volumes of aqueous vapor:

$$\underset{\text{2 vols.}}{2nH_2} + \underset{\text{1 vol.}}{nO_2} = \underset{\text{2 vols.}}{2nH_2O.}$$

According to the above, *two volumes of hydrogen and one volume of oxygen condense in their union to two volumes of aqueous vapor.*

These conclusions are confirmed by the following experiments:

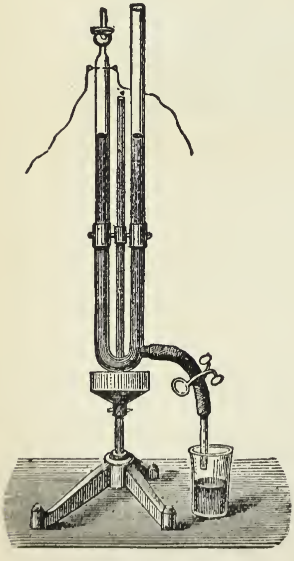


FIG. 47.

1. When water is decomposed by the electric current in a voltameter, or, more suitably, in Hofmann's apparatus (Fig. 38, p. 77), it will be found that the volume of the separated hydrogen is double that of the oxygen. This can also be proved synthetically. Introduce 1 volume of oxygen and 2 volumes of hydrogen into a eudiometer tube filled with mercury (see Air), and let the

electric spark pass through the mixture. This will unite the two gases, a small quantity of water forming at the same time; all the gas has disappeared, and the tube is completely filled with mercury. In place of the eudiometer, the apparatus (devised by Hofmann) pictured in Fig. 47 may be advantageously employed in this experiment (and also in many others). It consists of a U-shaped glass tube, one limb of which, open above, is provided below with an exit tube. The other limb really represents a eudiometer; it is divided into cubic centimeters. It has two platinum wires fused into the upper end, and provided with a stop-cock to admit and let out the gases and thus test them. Fill the tube to the stop-cock with mercury, and run into the eudiometer limb 1 volume of oxygen and 2 volumes of hydrogen. The side exit tube serves to run out the mercury to the same level in both tubes, so that the gases are always measured under the same atmospheric pressure, and thus their volumes are easily compared.

2. To determine the volume of the resulting water existing as aqueous vapor it is only necessary, after the explosion, to convert it by heat into steam. The apparatus (Fig. 48) will answer for this purpose. This is essentially the same as that pictured in Fig. 47, with the eudiometer limb closed above and surrounded by a wider tube. Through the latter conduct the vapors of some liquid boiling above 100° C. (toluene, xylene or aniline). These, then, pass through the envelope *B*, and are again condensed in the spiral tube *C*. The quantities of hydrogen and oxygen used are heated to the same temperature, their volume noted, the explosion produced, and the volume of the resulting aqueous vapor determined. From this it is found that the volume of hydrogen is ⅔ of the volume of the gas mixture; and 3 volumes of oxyhydrogen gas yield 2 volumes of aqueous vapor.

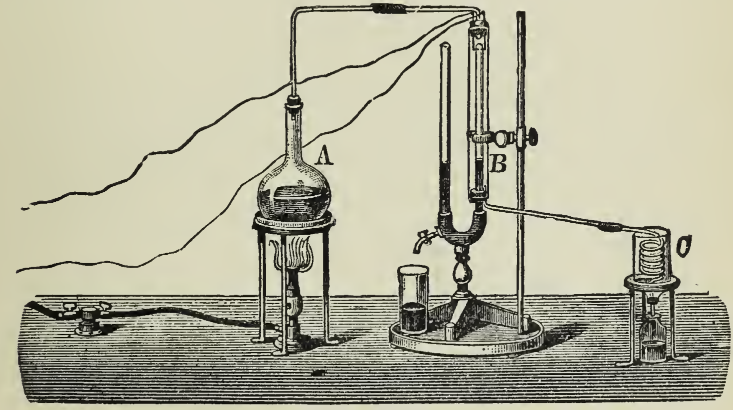


FIG. 48.

2. HYDROGEN PEROXIDE.

$H_2O_2 = 34.02$.

In addition to water, oxygen forms another compound with hydrogen, known as hydrogen peroxide. It was discovered by Thénard in 1818. It is produced by the action of dilute acids upon certain peroxides, such as those of sodium, calcium and barium. It is usually obtained by the action of hydrochloric acid upon barium peroxide:

$$\underset{\text{Barium peroxide.}}{BaO_2} + 2HCl = \underset{\text{Barium chloride.}}{BaCl_2} + H_2O_2.$$

Barium peroxide made to a paste with a little water (better, the hydrate—see Barium) is introduced gradually, in small quantities, into cold hydrochloric acid, diluted with 3 volumes of water. Hydrogen peroxide and barium chloride result; both are soluble in water. To remove the second from the solution, add to the latter a solution of silver sulphate as long as a precipitate is formed. Two insoluble compounds, barium sulphate and silver chloride, are produced by this reagent:

$$BaCl_2 + Ag_2SO_4 = BaSO_4 + 2AgCl.$$

Remove the precipitate by filtration and concentrate the aqueous solution. It now contains only hydrogen peroxide.

In making the peroxide, carbon dioxide may be allowed to act on barium peroxide suspended in water:

$$BaO_2 + CO_2 + H_2O = BaCO_3 + H_2O_2.$$

The insoluble barium carbonate is filtered off and the filtrate concentrated.

Hydrogen peroxide is most practically obtained by adding moist barium hydrated peroxide (see Barium) to cold dilute sulphuric acid. The reaction occurs according to the following equation:

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

When the acid is almost neutralized, filter the solution, and from the filtrate carefully precipitate the slight quantity of free sulphuric acid with a dilute barium hydroxide solution, then concentrate the liquid. Dry commercial peroxide of barium is not applicable for the above. A dilute solution of hydrogen peroxide is very readily prepared, if sodium peroxide (obtainable by fusing sodium in the air) is added to dilute tartaric acid.

A 45 per cent. solution can be readily made by evaporating the dilute aqueous hydrogen peroxide solutions on a water-bath at a temperature not exceeding 70°. The loss will be very slight. By extracting such a solution with ether and allowing the latter to evaporate a more concentrated product can be obtained and finally an almost anhydrous peroxide will remain.

The simplest means of preparing very pure hydrogen peroxide (99.7 per cent.) consists in distilling the aqueous solution (for example, the commercial 3 per cent. solutions) under reduced pressure. At 84–85°, under 68 mm. pressure, or at 69.2° and 26 mm. pressure, almost perfectly anhydrous hydrogen peroxide distils over [Wolffenstein, Ber. **27** (1894), II, 3307; Spring, Zeit. f. anorg. Chem. **8** (1895), 424; Brühl, Ber. **28** (1895), II, 2847.]

Besides these decompositions of metallic peroxides, other methods exist for preparing hydrogen peroxide (in small quantity). Thus, it arises frequently in slow oxidations, when ozone is also produced. If phosphorus, covered with water, be allowed to oxidize in the air, hydrogen peroxide will be found in the water, and the surrounding air will contain ozone (p. 85). Or, if a flask filled with air be shaken with zinc and water or dilute sulphuric acid, hydrogen peroxide will be produced. It is destroyed again by the prolonged action of the zinc. If zinc amalgam, in the presence of milk of lime, be shaken with caustic potash, calcium peroxide, CaO_2, will be at once precipitated. Copper, lead, iron, and other heavy metals do the same when agitated with more or less dilute sulphuric acid, and we find the same result by the oxidation of many organic substances, *e. g.*, pyrogallic acid and tannin on exposure to the air. In combustions, if the flame be cooled suddenly, we have formed, very often, slight quantities of hydrogen peroxide (and ozone), *e. g.*, in bringing a hydrogen or carbon monoxide flame in contact with water (Traube, Ber. 26 (1893), II, 1471, 1476). The explanation offered for this formation of hydrogen peroxide (and ozone) is, that in the oxidations, the oxygen molecules are torn asunder, and the nascent oxygen atoms oxidize the water to a slight degree to hydrogen peroxide, and oxygen to ozone. The rare occurrence of ozone is due either to its difficult formation, or to the fact that it is readily decomposed by the reacting bodies (zinc, etc.). This is also the case with hydrogen peroxide. The appearance of hydrogen peroxide in the oxidation of phosphorus seems to prove that it can be formed by *the oxidation of water*. This seems to be confirmed by its production on shaking turpentine oil with water and air, or if ozone be conducted into ether, and the ozonized product shaken with water. It appears probable, however, that in some oxidation reactions, the formation of the hydrogen peroxide is a consequence of the *reduction* of oxygen (Hoppe-Seyler and Traube). It may, for example, be assumed that when zinc (lead, iron) is shaken with air and water (or dilute sulphuric acid), the latter is decomposed in such a manner that the hydroxyl group combines with the zinc to hydroxide, and the liberated hydrogen then yields hydrogen peroxide with oxygen:

$$Zn + 2OHH + O_2 = Zn(OH)_2 + H_2O_2.$$
$$Zn + H_2O_2 = Zn(OH)_2.$$

A confirmation of this supposition is found in the electrolysis of water, where we discover hydrogen peroxide appearing at the negative pole (where hydrogen is found) if air or oxygen be conducted through the solution, $2H + O_2 = H_2O_2$. It is verified, too, in the production of hydrogen peroxide upon shaking palladium hydride with water and air (Traube):

$$Pd_4H_2 + O_2 = 4Pd + H_2O_2.$$

The excess of palladium hydride further decomposes the peroxide which was formed:

$$Pd_4H_2 + H_2O_2 = 4Pd + 2H_2O.$$

In all these examples we can explain the formation of the peroxide by the action of nascent hydrogen upon oxygen. It is, however, not true that hydrogen peroxide is formed only by the reduction of molecular oxygen (see above). An evidence of this is the fact that hydrogen peroxide is produced at the anode in the electrolysis of sulphuric acid; its appearance here is due to the decomposition of the persulphuric acid ($H_2S_2O_8$) (Richarz).

The production of hydrogen peroxide in oxidations has led to the assumption that *all* oxidations are conditioned by the transitory formation of hydrogen peroxide—*Traube's oxidation theory*. It was supposed that the proof of this could be found in the circumstance that various oxidations, *e. g.*, the union of carbon monoxide with oxygen to form carbon dioxide, could only occur with ease in the presence of aqueous vapor (Dixon): $CO + 2OHH + O_2 = CO_2 + H_2O + H_2O_2$. More careful investigations have, however, demonstrated that the presence of moisture is not absolutely essential in oxidations. Carbon monoxide and oxygen also combine to carbon dioxide when perfectly dry if the temperature be sufficiently high. Their union in the presence of moisture is due solely to the fact that the following transpositions, $CO + H_2O = CO_2 + H_2$ and $2H_2 + O_2 = 2H_2O$, take place more readily and at a lower temperature than the direct union of carbon monoxide with oxygen: $2CO + O_2 = 2CO_2$ (Lothar Meyer; see p. 92).

Hydrogen peroxide, concentrated as much as possible under diminished pressure, is a colorless, syrupy liquid which is blue in color in a thick layer. It does not congeal as readily as water. Its specific gravity at 15°, referred to water at the same temperature, is 1.49. It vaporizes on exposure to the air. It produces a burning sensation and white spots when applied to the skin. It sometimes explodes spontaneously with great violence. Its aqueous, rather concentrated solutions react acid and have a bitter, astringent taste. Hydrogen peroxide is not nearly so sensitive to heat as was formerly supposed, provided that all alkaline-reacting compounds and chemically active solids are absent. It is miscible in all proportions with water. Mixtures of the composition $H_2O_2 + H_2O$ and $H_2O_2 + 2H_2O$ solidify below —20°. Upon warming solutions containing more than 40 per cent. of hydrogen peroxide, the latter volatilizes in large amounts with the aqueous vapor and for the most part without decomposition (Wolffenstein, p. 100).

In concentrated solutions, it is very unstable, and easily decomposed with liberation of oxygen; in more dilute acidulated solutions it may be preserved longer. According to Spring, substances such as ether and alcohol, which reduce the surface tension of the liquid, tend to make its solution more durable, whereas bodies like caustic potash, etc., which increase the surface tension, hasten the breaking down of the hydrogen peroxide. In consequence of its ready decomposition, hydrogen peroxide oxidizes powerfully, since oxygen appears *in statu nascendi* (p. 53). It converts selenium, chromium, and arsenic into their corresponding acids; sulphides are changed to sulphates (PbS to $PbSO_4$); from lead acetate solutions the peroxide is precipitated, but is again decolorized by the excess of hydrogen peroxide. Organic dyestuffs are decolorized and decomposed. From hydrogen sulphide, sulphur, from hydrogen chloride and iodide, chlorine and iodine are set free:

$$H_2O_2 + 2HI = 2H_2O + I_2.$$

Sulphurous acid is oxidized to sulphuric acid:

$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O.$$

Thus hydrogen peroxide acts in a manner analogous to ozone; in both there exists a loosely combined atom of oxygen, which can readily be transferred to other bodies.

Hydrogen peroxide acts very slowly upon a neutral potassium iodide solution, while ozone separates iodine at once; but if platinum-black, ferrous sulphate, or blood-corpuscles (see p. 88), be added to the solution, iodine immediately separates, and colors added starch-paste a deep blue.

In all these cases the action of hydrogen peroxide is oxidizing. Some substances, on the other hand, are *reduced* by it, oxygen separating at the same time; this is true of certain unstable oxides, peroxides, and the highest oxidations of some metals, like Mn_2O_7, and CrO_3. Thus, argentic, mercuric, and gold oxides are reduced to a metallic state with an energetic evolution of oxygen:

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

Lead peroxide is changed to lead oxide:

$$PbO_2 + H_2O_2 = PbO + H_2O + O_2.$$

In the presence of acids, the solution of potassium permanganate is decolorized and changed to a manganous salt (see below). In the same way chromic acid and its salts are altered to chromic oxide:

$$2CrO_3 + 3H_2O_2 = Cr_2O_3 + 3H_2O + 3O_2.$$

Ozone and hydrogen peroxide gradually decompose into water and oxygen:

$$O_3 + H_2O_2 = O_2 + H_2O + O_2.$$

Chlorine in aqueous solution is oxidized to hypochlorous acid by hydrogen peroxide, $Cl_2 + H_2O_2 = 2HOCl$, but is again reduced by an excess of the latter:

$$HClO + H_2O_2 = HCl + H_2O + O_2.$$

Finally, hydrogen peroxide may be decomposed into water and oxygen by many bodies, especially when the latter exist in a divided condition; they are not in the least altered. Gold, platinum, silver, manganese peroxide, and carbon act in this way. Such reactions, in which the reacting substances undergo no perceptible changes, are designated *catalytic* (*χαταλύω*, I open) (compare p. 102). In many cases these may be explained by the previous formation of intermediate products, which subsequently react upon one another. Thus, we can suppose that in the action of silver and gold upon hydrogen peroxide oxides first result, but these are afterward reduced by it in the manner mentioned above (see p. 87).

REACTIONS FOR THE DETECTION OF HYDROGEN PEROXIDE.

Hydrogen peroxide decomposes potassium iodide very slowly; in the presence of ferrous sulphate, however, iodine separates at once, and is recognized by the blue color it yields with starch-paste. In the same way guaiacum tincture, in the presence of ferrous sulphate, is immediately colored blue, and an indigo solution is decolorized. The most characteristic test for the peroxide is the following: introduce hydrogen peroxide into a chromic acid solution, add a little ether and shake thoroughly; the supernatant ethereal layer will be colored blue (compare Chromic Acid).

A solution of titanic acid in sulphuric acid (diluted strongly with water), is also a delicate reagent; it gives an orange-yellow color with traces of hydrogen peroxide. This reaction can also be applied in the presence of persulphuric acid.

Hydrogen peroxide is determined quantitatively by oxidation with potassium permanganate (see Manganese). The latter is added to the solution, acidified with sulphuric acid, until a permanent coloration occurs. The reaction proceeds according to the equation:

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2.$$

Or the liquid to be examined (rain-water) for hydrogen peroxide is shaken in a stoppered glass with a 5 per cent. solution of potassium iodide and some starch-paste, allowed to stand several hours, and the iodine which separates is then determined colorimetrically (Schöne).

Thermo-chemical Deportment.—The great reactivity of hydrogen peroxide, its various modes of formation and its transpositions are fully explained by its thermal relations. Compared with water, it, like ozone, is an endothermic compound, *i. e.*, it contains more energy than water: $(H_2O,O) = -23$ Cal. Therefore, its formation from the latter requires the addition of energy. Its production by the oxidation of water is exceptional, and occurs with difficulty. It loses energy (heat) and readily changes to more stable water. Like ozone, its oxidations proceed more energetically than those with free oxygen, because 23 Cal. more are disengaged.

The production of hydrogen peroxide by the transposition of barium peroxide and hydrochloric acid proceeds with the liberation of heat:

$$BaO_2 + 2HCl,Aq = BaCl_2,Aq + H_2O_2 \;.\;.\;. + 22.0 \text{ Cal.}$$

Hydrogen peroxide is similarly formed from other peroxides, *e. g.*, potassium, calcium, and zinc peroxides. The superoxides or dioxides of manganese and lead (MnO_2 and PbO_2) do not yield hydrogen peroxide with acids. This is due to the fact that they are differently constituted chemically from the other peroxides.

Hydrogen peroxide occurs in slight quantity in the air and is detected in almost all rain-water and in snow—but not in natural dew and frost. Its quantity varies from 0.5 to 1 milligram in a liter of rain. Its formation in the air is probably induced by the action of ozone upon ammonia, whereby ammonium nitrite, hydrogen peroxide, and oxygen result (Carius).

Analysis shows that hydrogen peroxide consists of 1.01 parts of hydrogen and 16 parts of oxygen; its simplest formula would therefore be HO. The difficult volatility of the compound, and the reactions already described, cause us to believe that the molecule of hydrogen peroxide is more complicated, and is expressed by H_2O_2. It is supposed that the peroxide is composed of two groups of OH, called *hydroxyl;* these are combined with each other: HO — OH.

2. SULPHUR.

Atom: $S = 32.06$. Molecule: $S_2 = 64.12$ (above 1000° C.).

Sulphur is distributed throughout nature, both free and in a combined state. In volcanic regions, like Sicily, it occurs free, and there it forms vast deposits, mixed with gypsum, calcite and marl. Its compounds with the metals are known as blendes or glances. In combination with oxygen and calcium it forms calcium sulphate, the widely distributed gypsum. It is also present in many substances of the vegetable and animal kingdoms—*e. g.*, in the albuminoid bodies. It is interesting to note that many bacteriæ and algæ contain as much as one-fourth of their weight of sulphur.

To obtain sulphur, the natural product in Sicily is arranged in heaps, covered with earth, and then melted, or it is distilled from earthen retorts. To further purify this crude commercial product it is redistilled from cast-iron retorts, and when in a molten condition is run into cylindrical forms—*stick sulphur.* If the sulphur vapors are rapidly cooled during distillation (which occurs by conducting them into a stone chamber through which cold air circulates), they condense to a fine yellow powder, known as *flowers of sulphur* (Flores sulphuris).

Sulphur may be obtained by heating the well-known pyrites (FeS_2) away from air contact.

Appreciable quantities of sulphur are obtained from the material used in purifying gas—Laming's substance (ferric hydrate, lime and sawdust; which finally contains iron sulphide and sulphur), as well as in the LeBlanc soda process (see Soda).

Free sulphur exists in several allotropic modifications (see p. 87).

1. *Ordinary octahedral* or *rhombic sulphur* exists in nature in beautiful, well-crystallized rhombic octahedra (p. 35). It is pale yellow, hard and very brittle; on rubbing, it becomes negatively electrified. The specific gravity of this variety equals 2.07. It dissolves with difficulty in alcohol and ether; but is more readily soluble in hydrocarbons and ethereal oils. The best solvents are sulphur monochloride (S_2Cl_2) and carbon bisulphide (CS_2); 100 parts of the latter at 22° dissolve 46 parts of sulphur. By slow evaporation of the solutions sulphur crystallizes in transparent, lustrous, rhombic octahedra, like those occurring in nature. It fuses at 114.5° C. to a yellow, mobile liquid, which upon further heating becomes dark and thick, and at 250° is so viscid that it cannot be poured from the vessel containing it. Above 300° it again becomes a thin liquid, boils at 448°, and is converted into an orange-yellow vapor.

2. The *prismatic* or *monoclinic sulphur* is obtained from the rhombic when the latter is heated to its point of fusion; on cooling, it generally assumes the monoclinic form (rhombic crystals separate at 90° from sulphur which has been heated beyond the point of fusion). The monoclinic crystals are best obtained as follows: Fuse sulphur in a clay crucible, allow it to cool slowly until a crust appears on the surface; break this open near the side and pour out the liquid portion. The walls of the crucible will be covered with long, somewhat curved, transparent, brownish-yellow needles, or prisms of the monoclinic system. The same are obtained when a solution of sulphur in carbon bisulphide is heated to 100°, in a sealed tube, and then gradually allowed to cool; monoclinic crystals at first separate, and later, at lower temperatures, rhombic octahedra. The monoclinic crystals separated from the solution are almost colorless and perfectly transparent.

Prismatic or octahedral crystals may be obtained from a supersaturated benzene solution of sulphur, by adding small fragments of the corresponding crystals to the solution.

This form of sulphur has a lower specific gravity (=1.96) and fuses above 120°. It is soluble in the same solvents as the rhombic variety. It is very unstable; the transparent prisms and needles become opaque and pale yellow at ordinary temperatures, and specifically heavier, and pass over into an aggregate of rhombic octahedra retaining the external prismatic form. Stick sulphur deports itself similarly; the freshly moulded sticks are composed of monoclinic prisms, but in time their specific gravity changes and they are converted into the rhombic modification.

3. *Soft, plastic sulphur* appears to consist of two modifications. It is obtained when sulphur heated above 230° is poured in a thin stream into water; it then forms a soft, fusible mass, of a yellowish-brown color,

and its specific gravity equals 1.92. In a few days it hardens, and is converted into the rhombic variety. At 95° the conversion is instantaneous and accompanied by the evolution of considerable heat. It is only partly soluble in carbon bisulphide, leaving an amorphous powder undissolved—amorphous insoluble sulphur. As it reverts to the rhombic at 100° molten sulphur must be quickly chilled in order to obtain much of it. It is also produced when light acts upon dissolved or fused sulphur, and in the decomposition of the halogen-sulphur compounds by water. Flowers of sulphur, obtained by cooling sulphur vapor quickly, are for the most part insoluble in carbon bisulphide.

On adding hydrochloric acid to polysulphide solutions of potassium or calcium, sulphur separates as a fine, white powder, known as *milk of sulphur* (Lac sulphuris):

$$K_2S_5 + 2HCl = 2KCl + H_2S + 4S.$$

This is amorphous, soluble in carbon bisulphide, and gradually passes into the rhombic form.

The existence of these various modifications of sulphur, like that of ordinary oxygen and ozone, may be attributed to the fact that the sulphur molecules do not, under all circumstances, consist of the same number of atoms. This supposition is confirmed by the deportment of sulphur vapor. The density of the latter at 500° has been found to equal 192 ($O_2 = 32$). The vapor density steadily diminishes with increase of temperature and becomes constant at 1000°, and equals 64. Since the atomic weight of sulphur equals 32, it follows that at 1000° its molecules consist of two atoms ($S_2 = 64 = 32 \times 2$). At lower temperatures the sulphur vapors appear to contain molecules consisting of more than two atoms; thus at 500°, where the vapor density equals 192, the molecule consists of six atoms. According to this the hexatomic sulphur molecules dissociate, on further heating, and break down into normal diatomic molecules; the dissociation begins at 700° and is complete at 1000° (see p. 93). Since, therefore, the sulphur molecules in vapor form consist of two atoms at very high temperatures and of more atoms at lower, we may assume that the molecules in the liquid and solid condition are more complicated, and that the various allotropic modifications are influenced by the number of atoms contained in the molecules. Other solid metalloids—*e. g.*, selenium, phosphorus, arsenic, carbon, and silicon—occur in different modifications. As yet we have no means of ascertaining the molecular size of the elements in liquid and solid conditions; there is much, however, favoring the idea that when free they consist of complex atomic groups. Another explanation of allotropy will be given in connection with the different varieties of phosphorus.

Chemical Properties.—In its chemical behavior sulphur is very similar to oxygen. It unites directly with most of the elements. It ignites and burns with a pale bluish flame, forming sulphur dioxide (SO_2) when heated to 260° in the air. This union with oxygen occurs gradually even at lower temperatures (about 180°); in the dark it is accompanied by a white phosphorescent flame. Nearly all the metals combine with it to form sulphides. By rubbing mercury, flowers of sulphur and water together, we obtain black mercury sulphide. A moist mixture of iron filings and sulphur glows after a time. Copper and iron burn in sulphur vapor.

The sulphides are analogous to the oxides, exhibit similar reactions, and in the main possess a similar composition, as may be seen from the following formulas:

H_2O,	Water.	H_2S,	Hydrogen sulphide.
KOH,	Potassium hydrate.	KSH,	Potassium sulphydrate.
BaO,	Barium oxide.	BaS,	Barium sulphide.
CO_2,	Carbon dioxide.	CS_2,	Carbon bisulphide.
K_2CO_3,	Potassium carbonate.	K_2CS_3,	Potassium sulphocarbonate.

COMPOUNDS OF SULPHUR WITH HYDROGEN.

1. HYDROGEN SULPHIDE.

$H_2S = 34.08$.

In nature hydrogen sulphide occurs principally in volcanic gases and in the so-called sulphur waters (p. 91). It is always produced in the decomposition of organic substances containing sulphur, particularly the albuminoids by which the sulphates, *e. g.*, gypsum, are reduced with the formation of hydrogen sulphide. Hence the occurrence of the gas in eggs, sewers, etc. It may be formed directly from its constituents, although in small quantity, if hydrogen gas be conducted through boiling sulphur, or if sulphur vapors, together with hydrogen, be conducted over porous substances (pumice-stone, bricks) heated to 500°. Many sulphides are reduced upon ignition in a stream of hydrogen, with separation of hydrogen sulphide:

$$Ag_2S + H_2 = 2Ag + H_2S.$$

For its production acids are allowed to act upon sulphides. Ordinarily iron sulphide and diluted sulphuric acid are employed; the action occurs at ordinary temperatures:

$$\underset{\text{Iron sulphide.}}{FeS} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Ferrous sulphate.}}{FeSO_4} + H_2S.$$

The operation is performed either in a Kipp apparatus (p. 42) or in the one pictured on p. 43. Hydrogen sulphide thus obtained contains admixed hydrogen, in consequence of metallic iron existing in the sulphide. The pure gas is obtained by heating antimony sulphide with concentrated hydrochloric acid:

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Properties.—Hydrogen sulphide is a colorless gas, having an odor similar to that of rotten eggs; inhaled in large quantities it has a stupefying effect, and is very poisonous. At medium temperatures it condenses under a pressure of 17 atmospheres (under ordinary pressure at —74°) to a colorless liquid of specific gravity 0.9, which boils at —63.5° under 760 mm. pressure, and at —91° solidifies to a white crystalline mass. It is 1.18 times heavier than air. One volume of water dissolves 3 or 4 times its volume of the gas; the solution possesses all the properties of gaseous hydrogen sulphide and is therefore called hydrogen sulphide water.

Ignited in the air the gas burns with a blue flame, water and sulphur dioxide resulting:

$$H_2S + 3O = H_2O + SO_2.$$

With insufficient air access, or when the flame is cooled by the introduction of a cold body, only hydrogen burns and sulphur separates out in a free condition. This behavior is utilized in the technical preparation of sulphur from soda residues. In aqueous solution hydrogen sulphide is similarly decomposed by the oxygen of the air at ordinary temperatures, sulphur separating as a fine powder:

$$H_2S + O = H_2O + S.$$

The halogens behave like oxygen; the hydrides of the halogens are formed with separation of sulphur:

$$H_2S + I_2 = 2HI + S.$$

This reaction, which occurs only in the presence of water, serves for the production of hydrogen iodide (p. 63).

As hydrogen sulphide has a great affinity for oxygen, it withdraws the latter from many of its compounds, and it therefore acts as a reducing agent. Thus chromic, manganic, and nitric acids are reduced to lower stages of oxidation. On pouring fuming nitric acid into a vessel filled with the dry gas, the mixture will unite with a slight explosion.

Hydrogen sulphide possesses weak acid properties, reddens blue litmus-paper, forms salt-like compounds with bases, and is, therefore, termed hydrosulphuric acid. Nearly all the metals liberate hydrogen from it, yielding metallic sulphides:

$$Pb + H_2S = PbS + H_2.$$

Wi h the oxides and hydroxides of the metals hydrogen sulphide yields sulphides and sulphydrates:

$$KOH + H_2S = \underset{\substack{\text{Potassium} \\ \text{hydrosulphide.}}}{KSH} + H_2O.$$

$$PbO + H_2S = \underset{\substack{\text{Lead} \\ \text{sulphide.}}}{PbS} + H_2O.$$

Sulphides, therefore, like the compounds of the halogens with the metals, may be viewed as the salts of hydrosulphuric acid. The sulphides of almost all the heavy metals are insoluble in water and dilute acids;

therefore, they are precipitated by hydrogen sulphide from solutions of metallic salts:

$$\underset{\text{Copper sulphate.}}{CuSO_4} + H_2S = \underset{\text{Copper sulphide.}}{CuS} + \underset{\text{Sulphuric acid.}}{H_2SO_4}.$$

The precipitates thus obtained are variously colored (copper sulphide, black; cadmium sulphide, yellow; antimony sulphide, orange), and answer for the characterization and recognition of the corresponding metals. Paper saturated with a lead salt solution is at once blackened by hydrogen sulphide, lead sulphide being formed—a delicate test for the gas.

Thermo-chemical Deportment.—Hydrogen sulphide is a feebly exothermic compound. When hydrogen gas unites with amorphous sulphur to form hydrogen sulphide 4.7 Cal. are developed. When the gas dissolves in much water its heat of solution equals +4.6 Cal., so that the total heat of formation of hydrogen sulphide in dilute aqueous solution is 9.3 Cal.:

$$(H_2,S - \text{gas}) = 4.7;\ (H_2S,Aq) = 4.6;\ (H_2,S,Aq) = 9.3.$$

It is because of this low heat of formation that the gas is produced with such difficulty from its elements, and it is for this reason that it is so readily dissociated by heat into its elements. Its entire chemical deportment is also accounted for by its heat of formation (p. 114).

MOLECULAR FORMULA OF HYDROGEN SULPHIDE. ATOMIC WEIGHT OF SULPHUR.

Considerations similar to those which led us to adopt the molecular formula H_2O for water impel us to accept the formula H_2S for hydrogen sulphide. Its gas density, its analysis, and the fact that in an equal volume of any sulphur-containing gaseous compound there has never been observed less sulphur than is contained in hydrogen sulphide speak in favor of the assumption. The atomic value of sulphur is therefore 32.06 (compare p. 97).

From the molecular formula H_2S we further conclude that the hydrogen contained in one volume of hydrogen sulphide would occupy in a free condition the same volume as the latter:

$$\underset{\text{1 vol.}}{nH_2S} \text{ contains } \underset{\text{1 vol.}}{nH_2}.$$

This conclusion is verified experimentally as follows: In a bent glass tube filled with mercury (p. 78, Fig. 41), introduce dry hydrogen sulphide gas; then in the bent portion place a piece of tin, which is heated by a lamp. The sulphur of the hydrogen sulphide combines with the metal to form solid tin sulphide, while hydrogen is set free; its volume is exactly equal to the volume of the employed hydrogen sulphide. The quantity of sulphur, 32 parts, in vapor form, at 1000°, when the density is 64 (p. 106) combined with hydrogen (2 parts) would equal exactly half the volume of the hydrogen; at 500°, however, when the vapor density is three times as great, it will equal one-sixth of the volume of the hydrogen. Written molecularly, we have:

$$\text{At } 500°: \underset{\text{1 vol.}}{S_6} + \underset{\text{6 vols.}}{6H_2} = \underset{\text{6 vols.}}{6H_2S}.$$

$$\text{At } 1000°\text{, however}: \underset{\text{1 vol.}}{S_2} + \underset{\text{2 vols.}}{2H_2} = \underset{\text{2 vols.}}{2H_2S}.$$

HYDROGEN PERSULPHIDE.

Just as hydrogen peroxide, H_2O_2, is formed by the action of acids upon some peroxide, so may hydrogen persulphide be obtained from metallic persulphides or polysulphides. Sodium and potassium each form four polysulphides which are available for this purpose. With sodium for example there are, in addition to the ordinary sulphide Na_2S, also the compounds Na_2S_2, Na_2S_3, Na_2S_4, Na_2S_5. For quite a while it was thought that these polysulphides were decomposed by dilute acids similarly to the decomposition of barium peroxide by dilute sulphuric acid:

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2,$$

that therefore each polysulphide had a corresponding hydrogen polysulphide. This idea was enforced by the fact that the alkaloid strychnine formed a crystalline product with H_2S_3, and brucine one with H_2S_2. Rebs, however, demonstrated that when the different polysulphides are decomposed it is probably always *hydrogen pentasulphide*, H_2S_5, which is produced. It is a light-yellow colored, transparent mobile oil with a peculiar odor. Its specific gravity equals 1.71 at 15°. When dry and away from air contact it decomposes slowly. Water resolves it quickly into hydrogen sulphide and sulphur, which separates. Heat induces the same decomposition:

$$H_2S_5 = S_4 + H_2S.$$

Rebs (see Ann. Chem. (1888) **246**, 354) explains the formation of hydrogen pentasulphide from the alkaline bi-, tri-, and tetrasulphides in the following equations:

$$4Na_2S_4 + 8HCl = 8NaCl + 4H_2S_4;\ 4H_2S_4 = 3H_2S_5 + H_2S.$$
$$4Na_2S_3 + 8HCl = 8NaCl + 4H_2S_3;\ 4H_2S_3 = 2H_2S_5 + 2H_2S.$$
$$4Na_2S_2 + 8HCl = 8NaCl + 4H_2S_2;\ 4H_2S_2 = H_2S_5 + 3H_2S.$$

COMPOUNDS OF SULPHUR WITH THE HALOGENS.

Sulphur and chlorine unite to form three compounds: SCl_2, SCl_4, and S_2Cl_2. It is only the last which meets with any practical application.

Sulphur Dichloride—SCl_2—is produced when sulphur monochloride, S_2Cl_2, is saturated with chlorine at 6° to 10°:

$$S_2Cl_2 + Cl_2 = 2SCl_2.$$

The excess of chlorine is removed by conducting a stream of dry carbon dioxide through it.

It is a dark-red colored liquid, with a specific gravity of 1.62; boils at 64°, with partial decomposition into S_2Cl_2 and Cl_2; the dissociation commences at ordinary temperatures.

Sulphur Tetrachloride—SCl_4—only exists at temperatures below 0° C. It is formed by saturating S_2Cl_2 with Cl at —20° to —22°. The dissociation commences at —20°, and is complete at +6°. It yields crystalline compounds with some chlorides—*e. g.*, $SnCl_4$, $AsCl_3$, $SbCl_3$.

The most stable of the sulphur chlorides is

Sulphur Monochloride—S_2Cl_2—which is formed when chlorine is conducted over molten sulphur contained in the flask *C* (Fig. 49). It distils over and condenses in the receiver *D;* the product is redistilled, to obtain it pure. [Fig. 49, *A:* chlorine generator; *B:* wash-bottle; *E:* entrance for water intended to chill the vapors.]

Sulphur monochloride is a reddish-yellow liquid with a sharp odor, provoking tears, having a specific gravity of 1.68, and boiling at 138°. Its vapor density equals 135 ($O_2 = 32$), corresponding to the molecular formula S_2Cl_2. It fumes strongly in the air, and is decomposed by water into sulphur dioxide, sulphur and hydrochloric acid:

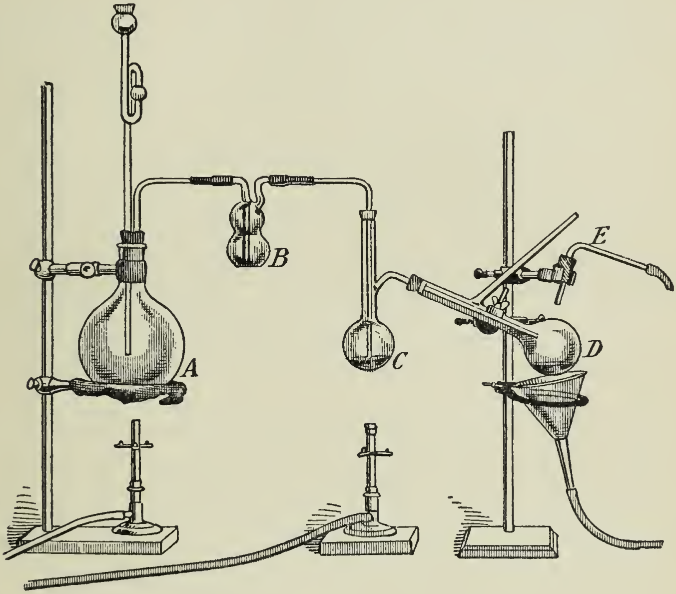


FIG. 49.

$$2S_2Cl_2 + 2H_2O = SO_2 + 4HCl + 3S.$$

Sulphur monochloride dissolves sulphur readily and serves in the vulcanization of caoutchouc.

Bromine forms analogous compounds with sulphur. S_2Br_2 is a red liquid, boiling at 190–200°. Compounds of iodine and sulphur are not definitely known.

3. SELENIUM.

Atom: $Se = 79.1$. Molecule: $Se_2 = 158.2$ (at 1400°).

This element is not very abundant in nature, and is only found in small quantities, principally in certain iron pyrites (in Sweden and Bohemia). Upon roasting this ore of iron, for the preparation of sulphuric acid, selenium settles out in the chimney dust or in the deposit of the lead chambers (compare Sulphuric Acid), and was found there by Berzelius in the year 1817. It was called selenium (*σελήνη*, moon) to indicate its relation to the already known tellurium (*tellus*, earth).

Like sulphur, selenium forms different allotropic modifications. *Amorphous selenium*, obtained by the reduction of selenium dioxide (SeO_2) by means of sulphur dioxide (SO_2), is a reddish-brown powder, soluble in carbon bisulphide, and has a specific gravity of 4.26. Selenium crystallizes from carbon bisulphide in brownish-red crystals of specific gravity 4.5. The solution of potassium selenide is brown-red, and when it is exposed to the air, black leaf-like crystals of selenium (with specific gravity 4.8) separate. These are isomorphous with sulphur and insoluble in carbon bisulphide. Upon suddenly cooling fused selenium it solidifies to an amorphous, glassy, black mass, which is soluble in carbon bisulphide and has a specific gravity of 4.28. When selenium (amorphous) is heated to 90–100°, its temperature suddenly rises above 200°; it is converted into a crystalline, dark-gray mass with a specific gravity of 4.8. It possesses metallic luster, conducts electricity, and is insoluble in carbon bisulphide. The *crystalline, insoluble modification* is obtained by slowly cooling the molten selenium.

Selenium melts at 217°, and boils at about 660°, passing into a dark-yellow vapor. The vapor density diminishes regularly with increasing temperature (similar to sulphur), and becomes constant at 1400°. It then equals 158; the molecule of selenium at 1400° consists of two atoms ($2 \times 79.1 = 158.2$).

Selenium resembles sulphur very closely in its chemical behavior. It burns in the air with a reddish-blue flame, forming selenium dioxide, and emits a peculiar odor resembling rotten horse-radish. It dissolves with a green color in concentrated sulphuric acid, and forms selenious and sulphurous acids:

$$Se + 2H_2SO_4 = SeO_2 + 2SO_2 + 2H_2O.$$

Hydrogen Selenide—H_2Se—produced, like hydrogen sulphide, from iron selenide and hydrochloric acid—is a colorless, disagreeably smelling gas with poisonous action. In the air the aqueous solution becomes turbid and free selenium separates.

With chlorine selenium forms $SeCl_4$ and Se_2Cl_2, perfectly analogous in general to the sulphur compounds but differing from them in that selenium tetrachloride is a solid which sublimes and does not begin to decompose until at about 200°.

4. TELLURIUM.

Atom : Te = 127. Molecule : Te_2 = 254 (at 1700°).*

Tellurium is of rare occurrence, either native or in combination with metals. It is associated with gold and silver in sylvanite, with silver and lead in altaite, and with bismuth in tetradymite. It is found principally in Transylvania, Hungary, California, Virginia, Bolivia, Brazil, and in the volcanic formations of the Liparian Islands.

The tellurium precipitated by sulphurous acid from a solution of tellurous acid is a black powder of specific gravity 5.9. It is silver-white when fused, of a perfect metallic luster, and conducts electricity and heat. It crystallizes in rhombohedra, having a specific gravity 6.4. It fuses at 452° and boils at 1390°. When heated in the air it burns, with a bluish-gray flame, to tellurium dioxide (TeO_2).

The vapor density of tellurium at 1400–1700° has been discovered to be about 254, corresponding to the molecular formula Te_2.

Hydrogen Telluride—H_2Te—formed by the action of hydrochloric acid upon zinc telluride, is a colorless, very poisonous gas, with disagreeable odor.

Two chlorides—$TeCl_2$ and $TeCl_4$, and two bromides, $TeBr_2$ and $TeBr_4$—have been formed. The tetrachloride boils at 380°. As its vapor density corresponds to the formula $TeCl_4$ the tellurium is quadrivalent.

SUMMARY OF THE ELEMENTS OF THE OXYGEN GROUP.

The elements oxygen, sulphur, selenium and tellurium form a natural group of chemically similar bodies. The similarity of the last three is especially marked, while oxygen, possessing the lowest atomic weight, stands somewhat apart. Among the halogens, fluorine exhibits a similar deportment ; it departs somewhat from its analogues, chlorine, bromine and iodine. Like the halogens the elements of the oxygen group present a gradation in their properties corresponding to their atomic weights :

	O	S	Se	Te
Atomic weights,	16	32.06	79.1	127.

With the increase in the atomic weight there occurs a simultaneous condensation of substance, the volatility diminishes, while the specific gravity and the points of fusion and boiling increase, as may be seen in the following table.

---

* The atomic weight of tellurium was first made 128 and subsequently 125. But the later development of the periodic system made it more probable that it was even lower than the atomic weight of iodine (126.8), which view has since been confirmed experimentally by Brauner. More recently results have been obtained which argue for the higher atomic weight, Te = 127. (See Staudenmaier, Zeit. f. anorg. Chem. **10** (1895), 189.)

	Oxygen.	Sulphur.	Selenium.	Tellurium.
Specific gravity, . .	1.124 (at —181°)	1.95–2.07	4.2–4.8	6.4
Melting point, . . .	.	114.5°	217°	452°
Boiling point, . .	—181°	440°	600°	1390°
Gas density, ...	32.00	64.12	158.2	254

Oxygen is a difficultly coercible gas, while the others are solids at ordinary temperatures. We must, however, bear in mind that sulphur, selenium and tellurium in a free state are probably composed of larger complex atomic groups (see p. 106).

Further, with rising atomic weight the metalloidal passes into a more metallic character. Tellurium exhibits the physical properties of a metal; even selenium possesses metallic properties in its crystalline modification. In chemical deportment, however, the metalloidal character shows scarcely any alteration.

All four elements unite directly, at elevated temperatures, with hydrogen, to compounds the composition of which is expressed by the general formula MH_2. At still higher temperatures these derivatives are again resolved into their elements. The similarity of water and the hydrides of sulphur, selenium and tellurium is restricted to their formulas. They are entirely different in their chemical nature. Water is absolutely necessary to life, while hydrogen sulphide, selenide and telluride are dangerous poisons. It must also occasion surprise that oxygen, the only gaseous member of the group, forms a derivative with hydrogen which is liquid at the ordinary temperature and a solid at 0°, whereas the hydrides of the elements sulphur, selenium and tellurium, volatile with difficulty, are also gaseous and are, comparatively speaking, condensed with more difficulty. It was indeed observed with the halogens that the hydride of fluorine, the most difficult to condense, possessed the highest boiling point, and we learned that the explanation for this was that, in accordance with its vapor density, hydrogen fluoride did not have the formula HF, but H_2F_2. Water also differs very much *thermo-chemically* from the hydrides of the other elements of the group. It is a strongly exothermic body, while hydrogen sulphide, on the other hand, formed from hydrogen and solid sulphur with the evolution of very little heat ($H_2,S =$ about 4 Cal.), and selenium and tellurium hydrides are indeed endothermic bodies.

This is a gradation similar to that observed in the halogen hydrides (p. 65). In accord with this we find that oxygen will displace these elements from hydrogen sulphide, hydrogen selenide, and hydrogen telluride when in aqueous solution with the formation of water. At higher temperatures and with an excess of oxygen the dioxides (SO_2, SeO_2) result. The halogens decompose them more readily than oxygen.

NITROGEN GROUP.

This group consists of nitrogen, phosphorus, arsenic, antimony, and bismuth. The last possesses a decidedly metallic character. It does not, like the other four elements, form gaseous derivatives with hydrogen. The gases argon, helium, metargon, krypton, xenon, and neon, occurring in the air, will be described in connection with nitrogen.

1. NITROGEN.

Atom: $N = 14.04$. Molecule: $N_2 = 28.08$.

Nitrogen exists free in the air, four-fifths by volume are nitrogen and one-fifth oxygen. In combination, it is chiefly found in the ammonium and nitric acid compounds, as well as in many organic substances of the animal and vegetable kingdoms.

Until 1894 it was thought possible to isolate nitrogen from the air by depriving the latter of its second constituent—oxygen. This is effected by bodies capable of absorbing oxygen without acting upon the nitrogen, *e. g*, phosphorus, hepar, alkaline solutions of pyrogallol and heated copper. The experiment can be most easily and simply performed in the following manner: Several pieces of phosphorus are placed in a dish swimming on water, ignited, and a glass bell-jar placed over them (Fig. 50). In a short time, when all the oxygen is absorbed from the air, the phosphorus will cease burning; the phosphorus pentoxide produced dissolves in the water, and the residual gas consists of almost pure nitrogen: its volume will equal four-fifths of the air taken. Another procedure consists in conducting air through a red-hot tube filled with copper turnings; the copper unites with the oxygen and pure nitrogen escapes. The portion of air remaining after these experiments was considered to be nitrogen until 1894 when Lord Rayleigh and W. Ramsay proved to the universal surprise that so-called "atmospheric nitrogen" was a mixture of nitrogen and argon. Lately, other very probably elementary gases have also been discovered in it.

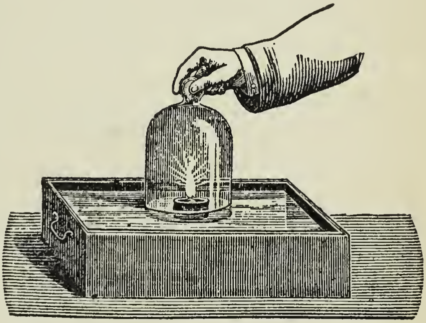


FIG. 50.

Pure nitrogen can only be obtained from nitrogenous chemical compounds. The following is a simple method to this end: Heat ammonium nitrite in a small glass retort; this decomposes the salt directly into water and nitrogen:

$$NH_4NO_2 = N_2 + 2H_2O.$$

In place of ammonium nitrite a mixture of potassium nitrite (KNO_2) and ammonium chloride (NH_4Cl) may be used; upon warming, these salts yield, by double decomposition, potassium chloride and ammonium nitrite ($KNO_2 + NH_4Cl = NH_4NO_2 + KCl$), which latter decomposes further. As potassium nitrite usually contains free alkali, some potassium bichromate is added to neutralize the same. Practically, the solution consists of 1 part of potassium nitrite, 1 part of ammonium chloride, and 1 part of potassium bichromate in 5 parts of water, and is then boiled; to free the liberated nitrogen from every trace of oxygen the gas is conducted over ignited copper.

The action of chlorine upon aqueous ammonia produces pure nitrogen. Ammonia is a compound of nitrogen and hydrogen. While the chlorine combines with the hydrogen of the ammonia to hydrochloric acid, nitrogen is liberated. The hydrochloric acid unites with the excess of ammonia to ammonium chloride (NH_4Cl). The following equations express the reactions:

$$2NH_3 + 3Cl_2 = N_2 + 6HCl$$

and

$$6HCl + 6NH_3 = \underset{\text{Ammonium chloride.}}{6NH_4Cl.}$$

The apparatus pictured on p. 50 will serve to carry out the experiment. The disengaged chlorine is conducted through a Woulff wash-bottle containing ammonia water, the free nitrogen being collected over water.

In this experiment the greatest care should be exercised that an excess of chlorine is not conducted into the solution, because its action upon the ammonium chloride will cause the formation of an exceedingly explosive body, nitrogen chloride, NCl_3 (p. 133), which separates in oily drops.

Properties—Nitrogen is a colorless, odorless, tasteless gas. One liter of it weighs 1.2507 grams at 0° and 760 mm. pressure. It is therefore 0.97 times as heavy as air. Its critical temperature lies near —146°, and its critical pressure equals 35 atmospheres (p. 48). Liquid nitrogen is colorless, boils under a pressure of one atmosphere at —194°, at —225° under a pressure of 4 mm., and has a specific gravity of 0.885 (at —194°). It solidifies at —214°.

In its chemical deportment it is extremely inert, combining directly with but few elements, *e. g.*, with oxygen and hydrogen under the influence of the electric spark; with magnesium and other metals at more elevated temperatures, and with lithium at the ordinary temperature. It does not support combustion or respiration; a burning candle is extinguished and animals are suffocated by it. This is not due to the activity of the nitrogen, but to the absence of oxygen—a substance which cannot be dispensed with in combustion and respiration. The presence of nitrogen in the air moderates the strong oxidizing property of the pure oxygen.

THE ATMOSPHERE.

The air, or the envelope encircling the earth, the atmosphere (*ἀτμὸς*—vapor; *σφαῖρα*—ball, sphere), consists principally of a mixture of nitrogen and oxygen; it always contains, in addition, slight and variable quantities of aqueous vapor, carbon dioxide, and traces of other substances, as accidental constituents (p. 123). Recently the gases *argon*, *helium*, *metargon*, *neon*, *krypton*, and *xenon* have been discovered in it. They occur in small amounts, but are constant constituents. The pressure exerted by the air is measured by a column of mercury which holds it in a state of equilibrium; the height of the barometric column at the sea-level and 0° C. equals, upon an average, 760 millimeters. As 1 c.c. of mercury weighs 13.6 grams, 76 c.c. will equal 1033.6 grams, and the last number would indicate the pressure which the column of air exerts upon one square centimeter of the earth's surface.

One cubic centimeter of air weighs, according to recent experiments, under normal conditions, 0.00129276 gram; 1000 c.c., therefore, or one liter, would weigh 1.29276 grams. As one liter of water weighs 1000 grams, air is consequently 773 times lighter than it. Air is 14.4 times heavier than hydrogen. Its density is 28.95 referred to $O_2 = 32$. Its specific volume is 773.4, *i. e.*, 1 gram of air at 0° and 760 mm. pressure occupies 773.4 c.c. (pp. 45, 79).

The *liquefaction of air*—or at least a portion of it—can be accomplished by the methods described on p. 48. Dewar and also Olszewsky chilled air, by means of boiling ethylene, almost to its critical temperature (—140°), and then liquefied it by a simultaneous, corresponding increase of pressure (75 atmospheres). Another less expensive method, hence well adapted for technical purposes, utilizes the great reduction in temperature sustained by strongly compressed gases when suddenly released from pressure. In the apparatus constructed almost simultaneously by Linde (Munich), Tripler (New York) and Hampson (London) the gas under slight pressure and cooled by sudden expansion is directed around a current of gas passing in an opposite direction under high pressure, whereby the temperature is eventually lowered below the critical temperature.

Liquid air is colorless. It is turbid, owing to the solid carbon dioxide from which it can be freed by filtration. Its boiling point (according to Dewar) is —190°, at which temperature almost pure nitrogen is evolved. The specific gravity of freshly prepared liquid air is 0.9951 referred to water at 4°. It contains much more oxygen than the gas. Recently prepared it holds as much as 54 per cent. of oxygen by weight, while the gas form has only 23 per cent. of oxygen by weight. Hence the name *liquid air* is not an entirely correct designation. The oxygen-content of liquid air increases by preservation. This may be accomplished by means of Dewar bulbs or double-walled tin or wooden boxes the air space of which is filled out with silk, etc. It will finally contain as much as 94 per cent. by weight of oxygen. This gradual accumulation of the gas in the liquid air is attributable to the fact that under the ordinary pressure nitrogen boils at —194°; oxygen, however, at —184°. There is here the greatest technical possibility, that by boiling out nitrogen from liquid air, almost pure oxygen can be prepared on a large scale.

The effect of low temperatures upon the physical properties of bodies and upon the course of chemical reactions can be well shown by means of liquid air. Carbon dioxide and acetylene solidify in it. The solid acetylene may be ignited; it then burns away like paraffin. Liquid air immediately solidifies mercury and renders it malleable. Alcohol at once forms drops in liquid air and soon becomes hard and crystalline. The hand may be plunged for a short period into the liquid of —190° without experiencing any ill effects, because it is at once surrounded by a protecting film. Dewar claims that the color of many bodies is changed if they are immersed in liquid air. Red mercuric oxide, iodide and sulphide (cinnabar) appear yellow in color, while the yellow-green nitrate of uranium appears white. Mention has already been made that chemical transpositions do not occur, or at least very slowly, at the temperature of liquid air (p. 28).

History.—It is well known that the air was formerly regarded as an element—a simple substance. However, observations were made very early which argue for the very opposite. As early as the ninth century certain chemists knew that the metals, when heated in air—*i.e.*, by calcination—increased in weight, and some of them correctly attributed this to the absorption of certain air particles by the hot metal. Because niter, like air, accelerates combustion, Hooke (seventeenth century) suspected that both contained an ingredient serving for combustion. It was especially the English chemists of the seventeenth century who busied themselves with researches in this direction. Mayow in particular deserves mention. He contended that the glowing metal united with the "spiritus nitro-aërus" of the air. He demonstrated that by respiration as well as by combustion the volume of air standing over water was diminished, and that the residuum—the destroyed air—was no longer available for respiration or combustion. However, these germs of the correct idea of combustion phenomena could not develop and grow under the predominance of the peculiar views then extant. Becher, a German chemist, began about 1700 to teach that the phenomenon of combustion originated in a peculiar volatile and escaping earth or kind of sulphur. His pupil Stahl, about 1720, developed this thought into a theory or doctrine, which held almost exclusive sway until near the closing third of the century. Stahl called the substance, which escaped in combustion, *phlogiston* (combustible). He failed to note that which became the main subject of investigation with the English chemists—that the burnt metal had increased in weight, and he explained that all combustible bodies consisted of phlogiston and a non-combustible substance. Thus, sulphur consisted of phlogiston and sulphuric acid, iron of ferric oxide and phlogiston, etc., etc. In the process of combustion the phlogiston escapes as flame and the non-combustible portion remains. The reduction of a metallic oxide by another metal or by a combustible body (*e. g.*, carbon) depends, therefore, upon the passage of phlogiston from the reducing to the reduced body; hence the terms—phlogisticated and dephlogisticated. The first corresponds to reduction and the second to oxidation. In this manner, because of the absence of more accurate experiments, the phenomena of combustion could be explained with some probability and apparent certainty. And Stahl became the founder of a chemical theory which lasted for more than a half century, and in its decadence found its most ardent advocates among the best and most celebrated English chemists of that period. Bayen (1774) showed that mercuric oxide was reduced without the addition of phlogiston (*i. e.*, by heating without the addition of carbon), and this led Lavoisier to his experiments upon the absorption of air in the calcination of the metals. He melted tin in a large, closed, air-tight flask. He had previously determined its weight as well as that of the tin. When the latter had become coated with a thick layer of oxide the apparatus was allowed to cool and was again weighed. Its weight was the same as at first, but when the flask was opened, air rushed in and the weight increased. Hence the tin, by calcination, had abstracted something from the air and had not, as required by the phlogiston theory, given anything to it. About this same period Scheele and Priestley discovered oxygen (p. 80), Rutherford (1742) had again described destroyed air, *i. e.*, nitrogen, and Scheele, by a series of excellent experiments, demonstrated the composition of air and the difference between nitrogen (aër mephiticus, aër vitalis) and carbon dioxide (aër aëreum). But he believed in the phlogiston theory. It was Lavoisier, during the same period, who clearly indicated and showed experimentally the rôle of oxygen in combustions and oxidations, and, shortly after, proved the elementary nature of nitrogen. Lavoisier named nitrogen *azote* (from ζώη, life, and *a*, privative), from which we get the symbol Az used in France for nitrogen. Chaptal was the first to give nitrogen the name nitrogenium (whence the symbol N), because it is a constituent of niter (nitrum). How English chemists have again extended our knowledge of the constituents of the air to a most unexpected degree may be gathered from pp. 115–123. Compare Berzelius' Lehrbuch der Chemie, 5 Aufl. (1843), 1, 140.

Quantitative Composition of Air.—Its composition is expressed by the quantity of oxygen, argon and nitrogen contained in it, as its remaining admixtures are more or less accidental and variable.

Boussingault and Dumas (1811) determined the accurate weight composition of the air (nitrogen and argon were of course calculated as "atmospheric nitrogen") by the following experiment: A large balloon, V, with a capacity of about 20 liters (Fig. 51), is connected with a porcelain tube, *a*, *b*, filled with metallic copper. Balloon and tubes, closed by stop-cocks, are previously emptied and weighed apart. The bent tubes, A, B, and C, contain caustic potash and sulphuric acid, and serve to free the air undergoing analysis from aqueous vapor, carbon dioxide, and other impurities. The porcelain tube, filled with copper, is heated to a red heat, and by carefully opening the stop-cocks *u*, *r*, and *r* a slow current of air is allowed to enter the empty balloon V. The impurities are given up in the bent tubes, and all the oxygen absorbed by the ignited copper, forming cupric oxide, so that only pure nitrogen enters V. Now close the cocks and weigh the balloon and porcelain tube, *a*, *b*. The increase in weight of the latter represents the quantity of oxygen in the air; the increase in V the quantity of nitrogen. In this manner Dumás and Boussingault found that in 100 parts by weight of air there are contained:

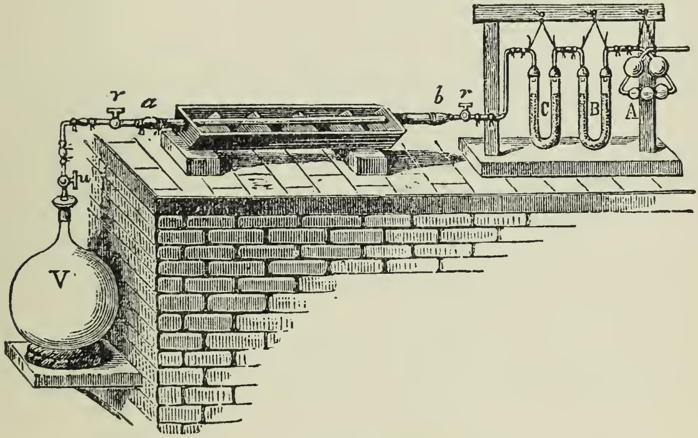


FIG. 51.

Nitrogen,	76.995	parts by weight.
Oxygen,	23.005	" " "
Air,	100.000	" " "

As a liter of oxygen weighs 1.4291 grams and a liter of atmospheric nitrogen 1.2571 grams the volume composition of air would be:

Oxygen,	20.8	parts by volume.
Nitrogen,	79.2	" " "
Air,	100.0	" " "

The density of air is 28.95 (p. 45) referred to oxygen equal to 32.

The volume composition of air may be directly found by means of the absorptiometer. The latter is a tube carefully graduated, and sealed at one end. This is filled with mercury, and air allowed to enter; the volume of the latter is determined by reading off the divisions on the tube. Now introduce into the tube, through the mercury, a platinum wire having a ball of phosphorus attached to the end (Fig. 52), or a ball of coke saturated with an alkaline solution of pyrogallic acid. The phosphorus absorbs the oxygen of the air, and only nitrogen remains, the volume of which is read off by the graduation.

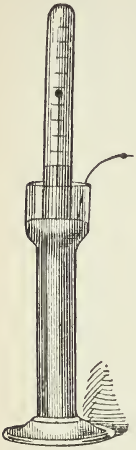


FIG. 52.

The *eudiometric method* affords greater accuracy. It is dependent upon the combustion of the oxygen with hydrogen in a eudiometer. Air and hydrogen are introduced into the eudiometer, and the electric spark then passed through the wires. All the oxygen in the air combines with a portion of the hydrogen to form water. On cooling, the aqueous vapor condenses and a contraction in volume occurs. Assuming that we had taken 100 volumes of air and 50 volumes of hydrogen, and that the residual volume of gas, after allowing for all corrections (p. 121), equaled 87.15; then of the original 150 volumes of mixed gas, 62.85 volumes disappeared in the formation of water. As the latter results from the union of 1 volume of oxygen and 2 volumes of hydrogen, the 100 volumes of air employed in the analysis therefore contained $\frac{62{\cdot}85}{3} = 20.95$ volumes of oxygen. Hence air consists (according to the determination of Regnault and Bunsen) of

79.05	volumes	Nitrogen.
20.95	"	Oxygen.
100.00	"	Air.

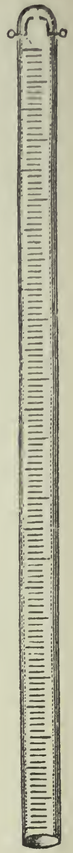


FIG. 53.

A eudiometer (εὐδία, fair weather, and μέτρον, measure—formerly it was thought that there was some connection between the quantity of oxygen in the air and the weather) is an absorptiometer, with two platinum wires fused into its closed end. The passage of the electric spark from wire to wire causes the explosion (Fig. 53).*

Numerous analyses show that the composition of the air everywhere on the earth's surface is constant. The most recent and exhaustive researches of Kreusler, Hempel, Morley, Rayleigh, and Leduc indicate it to be generally as follows:

---

* For further study of gasometric methods consult Rob. Bunsen, Gasometrische Methoden, 2 Aufl., 1877; Walther Hempel, Gasanalytische Methoden, 2 Aufl., 1890; Clemens Winkler, Lehrbuch der technischen Gasanalyse, 2 Aufl., 1892.

Nitrogen,	78.06	parts by volume ;	75.5	parts by weight.
Oxygen,	21.00	" " "	23.2	" " "
Argon,	0.94	" " "	1.3	" " "
	100.00	" " "	100.0	" " "

Measuring Gases.—The volume of gases is influenced by pressure, temperature, the moisture contained in them, and to a slight degree by their chemical nature. To compare statements of gas volumes, they must be recalculated to normal conditions, *i. e.*, it must be indicated what volume is occupied by the gas at 0° and 760 mm. barometric pressure. The pressure exerted by the mercury column of a barometer at a definite temperature depends not only on its height but also upon the intensity of gravity, which in turn varies with the latitude and sea-level. Hence it has been agreed to refer the "normal conditions" to 45° geographical latitude and the sea-level. The normal volume v_0 (at 760 mm. and 0°) is calculated, according to Boyle–Gay-Lussac's laws, from the volume v, which a gas occupies at pressure p and t^0 by the equation :

$$pv = p_0 v_0 \ (1 + \alpha t)$$

to be

$$v_0 = \frac{v \cdot p}{760\ (1 + \alpha t)}.$$

This answers only for dry gases. Any quantity of gas occupies less space when it is dry than when it is moist, because the tension of the aqueous vapor counteracts the atmospheric pressure.

The moisture may be removed by introducing into the gas a ball of coke saturated with sulphuric acid, which dries it. It is more convenient, however, to make the correction of the gas volume in the following manner : Water is brought in contact with the gas to be measured, in order to perfectly saturate it with aqueous vapor ; the gas is then measured and its normal volume calculated by the above formula, after deducting from the observed pressure p the number of millimeters corresponding to the tension of the aqueous vapor for the given temperature (p. 90). If the aqueous tension at t^0 be represented by s (mm. mercury) we finally reach the equation :

$$v_0 = \frac{v \cdot (p - s)}{760\ (1 + 0.003665 \cdot t)}.$$

Another form may be given the expression of the two laws relating to gases :

$$pv = p_0 v_0 \ (1 + \alpha t),$$

if the temperature be counted not from the melting of ice forward but from the *absolute zero* point of temperature, which can be developed from the following considerations. According to Gay-Lussac the volume of a gas increases, for every degree of rise in temperature, the 0.00367 or $\frac{1}{273}$ of the volume it occupied at 0°. If the temperature be lowered from 0° downward, and the law of Gay-Lussac continues to hold force, then the volume of the gas at —273° equals zero. This degree of temperature, which has been approached to within 30°, answers for the zero point of absolute temperature. It is indicated by the letter T. The relation between the degrees of absolute temperature and those of ordinary centigrade degrees is expressed by t = T —273. If this be introduced into the preceding equation we obtain

$$pv = \frac{p_0 \, v_0}{273} T,$$

or, if $\frac{p_0 \, v_0}{273}$ be made equal to R, then we have

$$pv = R \cdot T.$$

The value of R does not depend upon the chemical composition of the gas, but solely upon the units of measure chosen for p and v. The law of Avogadro can also be given expression through this equation if, following Horstmann's suggestion, consideration be given to the volumes which molecular quantities of the gases occupy,—*i. e.* the volume occupied by one molecule or 2.02 grams of hydrogen, 32 grams of oxygen, 70.9 grams of chlorine, 36.46 grams of hydrogen chloride. This volume is, consequently, 22.4 liters (p. 98). In this case R is the same for all gases. If the volume be measured in cubic centimeters, and the pressure in grams per square centimeter, then, as $v = 22400$, p would equal 1033.6 (p. 116), $T = 273$, and $R = 84800$.

The entire expression for the three laws would then read

$$pv = 84800\ T.$$

We shall see that this equation also possesses great value for solutions.

The Boyle–Gay-Lussac law is not an absolutely correct expression for the behavior of gases. At very great pressures they can be less compressed than would correspond to the requirements of the law. At low pressures, on the other hand, gases, hydrogen excepted, can be more strongly compressed than the law requires. These variations justify the theory propounded by the Hollander, van der Waals (1873). As the density of the gas increases the attraction between its molecules becomes greater and the outward pressure grows less; indeed, the diminution is inversely proportional to the square of the volume of the gas-mass. Accordingly, the observed pressure, when compared with that demanded by the law, is reduced about the value $\frac{a}{v^2}$, in which a is a constant corresponding to the attraction between the molecules—the cohesion of the gases. On the other hand, the space remaining, with the greater density, for the motions of the molecules is less than the observed volume, because we must deduct from the latter the space actually occupied by the molecules themselves. In calculation the observed pressure must therefore be increased and the observed volume must be diminished. This is indicated in the equation of van der Waals, mentioned on p. 49:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT.$$

or

$$\left(p + \frac{a}{v^2}\right)(v - b) = (1 + a)(1 - b)\frac{T}{273},^*$$

which not only answers for gases but also for liquids. The critical data of a gas may also be calculated from it.

From the great constancy of its composition air was supposed to be a chemical compound, consisting of nitrogen and oxygen. This supposition is, however, opposed by the following circumstances: All chemical compounds contain their constituents in atomic quantities, which is not the case with air. In the mixing of nitrogen and oxygen to form air there is neither disengagement nor absorption of heat, which is always observed in chemical compounds. Further, the air absorbed by water or other solvents possesses a composition different from the atmospheric; this is due to the unequal solubilities of nitrogen and oxygen in water. The air expelled from water upon application of heat consists of 34.9 volumes of oxygen and 65.1 volumes of nitrogen (Bunsen). These facts indicate that air is not a chemical compound, but a mechanical mixture of its two constituents (see Liquid Air).

The great constancy in the composition of our atmosphere is due chiefly to the fact that there is a constantly renewed mixture produced by the unceasing air currents, by winds and storms, rising of the warmer layers and the sinking of those which have become cooler. The mutual diffusion of gases comes, therefore, into consideration. The

---

[*] As $R = \frac{(1 + a)(1 - b)}{273}$ when $p = 1$ and $v = 1$.

gas molecules possess, as is now generally acknowledged, a direct, progressive, energetic movement, and can therefore diffuse without limitation into space if by contact with other molecules they are not deflected from or arrested in their course. This is the reason that two gases (or liquids) in immediate contact mix generally with one another. Another kind of diffusion—*transpiration*—need not be considered so far as concerns the constant composition of the atmosphere, but may be given as a conclusion to what has already been said. If two gases are separated by a permeable diaphragm or membrane, that one possessing the lower density will traverse the septum the more rapidly.

The following experiment very clearly illustrates this: In the open end of an unglazed clay cylinder (as used in galvanic elements) there is fixed a glass tube about one meter long, its open end terminating in a dish containing water; the cylinder and tube are filled with air. Over the porous cylinder is placed a wider vessel filled with hydrogen. The latter presses faster into the cylinder than the air escapes from it; the air in the tube and cylinder is displaced and rises in the water in bubbles. When the separation of gas ceases, tube and cylinder are almost filled with pure hydrogen. On removing the larger hydrogen vessel the gas will escape much more rapidly into the external air than the latter can enter the cylinder; the internal pressure will therefore be less than the external, and water ascends in the glass tube.

In addition to nitrogen and oxygen, air constantly contains aqueous vapor and carbon dioxide (CO_2) in very small quantities. The presence of the former can readily be recognized by the fact that cold bodies are covered with dew in moist air. Its quantity depends on the temperature and corresponds to the vapor tension of water (see p. 90). One cubic meter of air perfectly saturated with aqueous vapor contains 22.5 grams of water at 25° C.; on cooling to 0° 17.1 grams separate as rain. Generally the air contains only 50–70 per cent. of the quantity of vapor necessary for complete saturation. The amount of moisture in it is either determined according to physical methods (hygrometer), or directly by weighing. To this end a definite quantity of air is conducted through a tube filled with calcium chloride or sulphuric acid, and its increase in weight determined.

To detect the carbon dioxide in the air, conduct a portion of the latter through solutions of barium or calcium hydroxides, and a turbidity will ensue. To determine its quantity, pass a definite and previously dried amount of air through a weighed potassium hydrate tube, and ascertain the increase in weight of the latter. Ten thousand parts by volume of atmospheric air contain, ordinarily, from 3.0 to 4 parts by volume of carbon dioxide. (See Ber. **30** (1897), 1450.)

Besides the four ingredients just mentioned, air usually contains small quantities of ozone, hydrogen peroxide, ammonium salts (ammonium nitrite), the newly discovered gases *argon* and *helium*, and probably hydrogen. Finally, air contains microscopic germs of lower organisms; they are generally found in the lower air strata, and their presence influences the processes of decay and fermentation of organic substances.

GASES RECENTLY DISCOVERED IN THE ATMOSPHERE.

Lord Rayleigh in 1892, while engaged in an exhaustive research upon the density of the elementary gases, incidentally observed that a liter of nitrogen isolated from the air weighed 1.2571 grams under normal conditions, whereas a liter of the same gas prepared from ammonia or nitric acid weighed 1.2507 grams. The determined purpose of ascertaining the reason for this difference in the third decimal led Lord Rayleigh and

W. Ramsay in 1894 to the brilliant and surprising discovery of argon—a new constituent of the air, the composition of which, after the masterly investigations of eminent chemists, appeared to conceal from us no further enigmas. Yet, in March of 1895, as W. Ramsay sought for additional sources of argon, he found *helium*, a second apparently elementary gas, which, through a portion of its spectrum, had been known as a constituent of the sun. Prior to this it had not been certainly known to be present on the earth. It is a very subordinate constituent of the air, where it was first observed by Kayser. Ramsay obtained it by heating minerals containing uranium.

The two gases to which reference has just been made differ from all other gases known to us by the total absence of chemical activity. Thus far no other substance has been made to react with them. Hence the name Argon, from *ἀν ἐργον*, without action. They also differ from other gases in their real atomic structure; their atoms have not combined to molecules—a condition which heretofore has been observed only with other substances at very high temperatures (p. 79). This is evident from the relation of the specific heat at constant pressure to that at constant volume, which in the case of monatomic gases equals 1.67, whereas with polyatomic gases—those built up molecularly—the value lies between 1 and $\frac{5}{3}$. Compare O. E. Meyer, The Kinetic Theory of Gases (2d ed., 1895–1899).

Recently, Ramsay availed himself of the remarkably developed refrigatory apparatus and found four apparently elementary monatomic gases in air, while seeking for the one between argon and helium. He permitted large quantities of liquid argon and liquid air to boil away gradually, and then examined the more volatile portions and those portions not so readily volatile and more difficultly condensed. Thus he discovered in the residue, by the evaporation of 750 c.c. of liquid air to 70 c.c., the gas krypton (*κρυπτὸς*, concealed), which volatilizes with difficulty, has a density or atomic weight of 45 ($O_2 = 32$), and is characterized in its spectrum by a brilliant red, a yellow, and a green line, the last lying close to that of the northern light; similarly metargon and xenon (*ξένος*, foreign), both of which are present in the heavier portions of the air; and lastly the noncondensible, light neon (*νέος*, new), rich in lines, with the density 20, and probably the sought-for gas lying between argon and helium. No one of these four gases has been obtained in the pure state; therefore only argon and helium will be more fully discussed. (See Ramsay, Ber. 31 (1898), 3111.)

ARGON.

Atom: A = 40.

The air contains about 0.935 per cent. by volume of argon, while "atmospheric nitrogen" contains 1.183 per cent. by volume. We inhale daily about 20 liters of this enigmatical gas which has remained concealed for so long a time. It is present in many mineral waters and gases from springs, *e. g.*, those of Bath, Cauteret, Vöslau and Wildbad. It is liberated in small quantities, however, together with helium, upon heating certain minerals (especially those containing uranium)—cleveite, bröggerite, uraninite, and has been obtained in the same manner from one meteorite. Frequently the gases occluded in rock-salt contain argon.

Two methods may be pursued in separating argon from the air:

1. Air—freed from oxygen, aqueous vapor and other admixtures—"atmospheric nitrogen"—(p. 119) is conducted over red-hot magnesium filings, which absorb the nitrogen, forming magnesium nitride: $N_2 + Mg_3 = Mg_3N_2$ (p. 116), while the argon is scarcely acted upon. The nitrogen can be more quickly absorbed by lithium or by a heated mixture of magnesium and calcium oxide or finely divided calcium:

$$Mg + CaO = MgO + Ca.$$

Ramsay employed this method.

2. Lord Rayleigh mixed "atmospheric nitrogen," the mixture of nitrogen and argon, with oxygen and allowed the induction spark to pass continuously through this mixture in the presence of caustic potash. Alkaline nitrite is formed in this way from the nitrogen, oxygen and alkali (see Nitrous Acid, pp. 205, 207), while the residue of argon and oxygen is conducted over ignited copper to remove the latter. Cavendish, as early as 1785, observed that there remained some "atmospheric nitrogen" which was not converted into alkaline nitrite; he did not, however, pursue this observation further.

The argon thus prepared contains helium and neon as the lighter and metargon, krypton and xenon as the heavier admixtures. It is then liquefied by means of liquid air and purified by fractional distillation. Its density referred to $O_2 = 32$ is 39.914 or in round numbers 40; it is identical with its atomic weight. Under normal conditions a liter of argon weighs 1.780 grams. At very low temperatures it congeals to an ice-like mass, which melts at —189.5° to a colorless liquid. It boils at —185°; its critical temperature is —121° and its critical pressure 50.6 atmospheres. Argon is approximately 2½ times as soluble in water as nitrogen: 100 volumes of water dissolve 4 volumes of argon at 12°. Hence argon accumulates in the gases of rain-water. The spectrum distinguishes argon very certainly from nitrogen and other substances [compare: Z. f. phys. Ch. 1895, 16, 344; Z. f. anorg. Ch. 18 (1898), 222; Chem. Centralblatt 70 (1899), 1, 469; also Mugdan: Argon and Helium, two new gaseous elements, Stuttgart, 1896].

HELIUM.

Atom: He = 4.

Helium is as inactive chemically as argon. While the latter is widely distributed on the earth, helium is one of the rarest of terrestial substances. It occurs, however, with hydrogen in immense masses in the photosphere of the sun and other brilliant fixed stars. Norman Lockyer detected it as early as 1868 by means of the spectroscope in the chromosphere of the sun, and in 1869 he and Frankland named it Helium. In 1892 Palmieri observed its terrestial occurrence for the first time while studying spectroscopically a substance which had been thrown out by Vesuvius. But it was first in March, 1895, that W. Ramsay found helium while he was engaged in seeking for sources of argon. Hitherto only a portion of the helium spectrum (line D_3) had been known. The gas helium (together with hydrogen, carbon dioxide, nitrogen and probably also argon) is evolved when certain rare minerals, usually consisting of salts of uranium, yttrium and thorium (*e. g.*, cleveite, uraninite, bröggerite, monazite) are heated alone with dilute sulphuric acid (1 : 8) or with sodium bisulphate. It was similarly obtained from a meteorite. Kayser found it, in small quantities it is true, in the air and the later investigations of Ramsay and Travers have confirmed this observation. Helium, like argon, occurs in the gases from springs, *e. g.*, in those from Wildbad, in that of Adano near Padua, as well as in the gaseous exhalations of Tuscany.

Helium is monatomic (see above). Its atomic weight (its density) equals about 4. Dewar has shown that it can be liquefied by means of liquid, vaporizing hydrogen, so that at present all gases, with the exception of neon, can be liquefied. It is less soluble in water than any other gas: 100 volumes of water at 18° take up but 0.73 volume of helium. It is as inactive as argon. Travers asserts that when a powerful electric discharge is sent through a Plücker tube (see Spectrum Analysis) filled with helium the latter is absorbed by the platinum electrodes and is again liberated from the same on the application of heat. This recalls the behavior of hydrogen and palladium; it may be useful in separating helium and argon. Five brilliant lines are prominent in the spectrum of helium: one each in the red, the yellow, the green, the blue and the violet. The yellow line D_3 lies close to the two sodium lines, D_1 and D_2, toward the violet end of the spectrum.

COMPOUNDS OF NITROGEN WITH HYDROGEN.

Ammonia is the most important compound of nitrogen and hydrogen. It has been known for the longest time. Since 1889 Th. Curtius has added four other derivatives of these two elements to it: *hydrazine*, N_2H_4, and *hydrazoic acid*, N_3H, as well as the ammonium and hydrazine salts of the latter: N_4H_4 ($= NH_3 + N_3H$) and N_5H_5 ($= N_2H_4 + N_3H$). See Ber. 29 (1896), 759. *Oxyammonia* or *hydroxylamine*, NH_3O, discovered by W. Lossen in 1865, will be discussed after ammonia.

1. AMMONIA.

Molecule: $NH_3 = 17.07$.

Ammonia occurs in the air in combination with some acids, in natural waters and in the earth, but always in small quantities. Priestley first studied it carefully and called it alkaline air. Berthollet determined its composition in 1785. The formation of ammonia by the direct union of nitrogen and hydrogen occurs under the influence of the silent electric discharge. Its compounds—ammonium salts—are frequently produced under the most varying conditions. Thus ammonium nitrate is formed by the action of the electric spark upon moist air:

$$N_2 + O + 2H_2O = \underset{\text{Ammonium nitrate.}}{NH_4NO_3}.$$

Ammonium nitrite, NH_4NO_2, is said to be formed in every combustion in the air; and in the electrolysis of water. Further, ammonium salts are produced in the solution of many metals in nitric acid, in consequence of a reduction of the acid by the liberated hydrogen:

$$HNO_3 + 8H = 3H_2O + NH_3.$$

The following conversion of nitrogen into ammonia deserves consideration: Nitrogen unites with magnesium at a red heat to magnesium nitride, Mg_3N_2, and the latter is energetically decomposed by water with the evolution of ammonia:

$$Mg_3N_2 + 3H_2O = 3MgO + 2NH_3 \text{ (p. 124)}.$$

Nitric acid in the form of salts, in alkaline solution, is reduced by nascent hydrogen to ammonia (see Nitric Acid).

Ammonia is produced in large quantities in the decomposition and dry distillation of nitrogenous organic substances. Even as late as the last century the bulk of the ammonium chloride (the most important salt technically), was obtained from camel's dung or decayed urine. Its original name *Sal armoniacum*—Armenian salt—was confounded later with the designation for Egyptian rock-salt—*Sal ammoniacum*. In the preparation of illuminating gas by the distillation of coal, ammonia appears as a by-product and may be obtained by combining it with sulphuric or hydrochloric acid. This method is used almost exclusively at present for its production.

To prepare ammonia heat a mixture of ammonium chloride and slaked lime in a glass or iron flask:

$$\underset{\text{Ammonium chloride.}}{2NH_4Cl} + \underset{\text{Calcium hydroxide.}}{Ca(OH)_2} = CaCl_2 + 2H_2O + 2NH_3.$$

The disengaged ammonia gas is collected over mercury, as it is readily soluble in water (see p. 58, Fig. 33). For perfect drying conduct it through a vessel filled with burnt lime (CaO). Calcium chloride is not applicable for this purpose, as it combines with the gas. In consequence of its levity, ammonia, like hydrogen, may be collected by displacing the air in inverted vessels.

Physical Properties.—Ammonia is a colorless gas with a suffocating, characteristic odor. Its density is 0.59 (air = 1). Under a pressure of 6.5 atmospheres (at 10° C.), or by cooling to —40° C., under ordinary pressure it condenses to a colorless mobile liquid with a specific gravity of 0.623 at 0°, solidifies at —85°, and melts again at —75°. Liquid ammonia has recently been introduced into commerce.

Ammonia gas may be condensed, just like chlorine. Take ammonium silver chloride ($AgCl . 2NH_3$), obtained by conducting ammonia over silver chloride, and enclose it in a tube with a knee-shaped bend (p. 51, Fig. 32). The limb containing the compound is now heated in a water-bath, while the other limb is cooled. The compound is decomposed into silver chloride and ammonia, which condenses in the cooled limb (Faraday).

Ammonia gas dissolves very readily in water, with the liberation of heat. One part of water at 0° and 760 mm. pressure absorbs 1146 volumes (= 0.875 parts by weight); at 20°, 739 volumes (= 0.526 parts by weight) of ammonia. At 16° and 760 mm. pressure 100 parts by volume of water absorb 60 parts by weight of ammonia. The specific gravity of a 34.95 per cent. solution at 15° is 0.882; hence a liter of it contains 308.3 grams of ammonia. When a long glass tube, closed at one end and filled with ammonia, has its open end placed in water, the latter rushes up into the tube as it would into a vacuum; a piece of ice melts rapidly in the gas. The aqueous solution possesses all the properties of the free gas, and is called *Liquor ammonii caustici.* The greater the ammonia content the less will be the specific gravity of the solution. All the gas escapes on the application of heat.

When the condensed liquid ammonia evaporates it absorbs a great amount of heat, and answers, therefore, for the production artificially of cold and ice in Carré's apparatus. The simplest form of the latter is represented in Fig. 54. The iron cylinder *A* is filled about half with a concentrated aqueous ammonia solution, and is connected, by means of the tubes from *b*, with the conical vessel *F*, in the middle of which is the empty cylindrical space *E*. The entire internal space of *A* and *F* is hermetically shut off. *A* is heated upon a charcoal fire until the thermometer *a*, in it, indicates 130° C., while *F* is cooled with water. In this way the gaseous ammonia is expelled from the aqueous solution in *A*, passes through *b*, in which most of the water runs back, and condenses to a liquid in *B*, of the receiver *F*. The cylinder *A* is removed from the fire, cooled with water and the vessel *D*, constructed of thin sheet-metal and filled with water, placed in the cavity *E*, which is surrounded with a poor conductor, *e. g.*, felt. The ammonia condensed in *B* evaporates, and is reabsorbed by the water in *A*. By this evaporation a large quantity of heat, withdrawn from *F* and its surroundings, becomes latent; the water in *D* freezes.

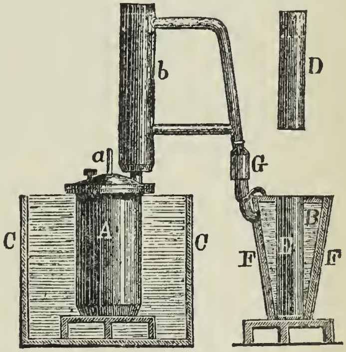


FIG. 54.

The method of Carré for the artificial production of ice has acquired great application in the arts; recently, however, ice machines have been introduced. These are driven by liquid ammonia (Linde), or by liquid sulphur dioxide and carbon dioxide (Pictet) (compare pp. 48, 117). The method of Windhausen, depending upon the expansion of compressed air, is much used.

Chemical Properties.—A red heat or the continued action of the electric spark decomposes ammonia into nitrogen and hydrogen. On conducting ammonia gas over heated sodium or potassium, the nitrogen combines with these metals and hydrogen escapes:

$$NH_3 + 3K = NK_3 + 3H.$$

Magnesium unites, when heated in an atmosphere of ammonia, with the nitrogen of the latter, giving a bright light:

$$3Mg + 2NH_3 = Mg_3N_2 + 3H_2.$$

Ammonia will not burn in the air; in oxygen, however, it burns with a yellow flame:

$$2NH_3 + 3O = N_2 + 3H_2O;$$

ammonium nitrite and nitrogen dioxide are formed simultaneously. When a mixture of ammonia and oxygen is ignited it burns with explosion.

To show the combustion of ammonia in oxygen, proceed as follows: A glass tube, through which ammonia is conducted, is brought with oxygen into a vessel, bringing the opening of the latter near a flame at the moment of the introduction of the glass tube. In contact with oxygen, the ammonia gas ignites and continues to burn in it.

The following experiment (of Kraut) shows the combustion of ammonia very conveniently. Place a somewhat concentrated ammonia solution in a beaker glass; heat over a lamp, until there is an abundant disengagement of gas, and then run in oxygen, by means of a tube dipped into the liquid. Upon approaching the mixture with a flame, it ignites with a slight explosion. The ignition may be induced without a flame, by sinking a glowing platinum spiral into the mixture; we then have a number of slight explosions. The glass is filled at the same time with white vapors of ammonium nitrite (NH_4NO_2); later, when oxygen predominates, red vapors of nitrogen dioxide (NO_2) and nitrous acid appear.

If chlorine gas be conducted into the vessel with ammonia, it immediately ignites and continues to burn in the latter, with the production of white fumes of ammonium chloride (NH_4Cl). The chlorine combines with the hydrogen of the ammonia, with separation of nitrogen, and yields hydrochloric acid, which unites, with the excess of ammonia, to form ammonium chloride:

$$NH_3 + 3Cl = 3HCl + N$$

and

$$3NH_3 + 3HCl = 3NH_4Cl.$$

Chlorine reacts similarly upon aqueous ammonia (p. 116).

In gaseous form, as well as in solution, ammonia possesses strong basic properties; it blues red litmus-paper and neutralizes acids, forming salt-like compounds with them, which are very similar to the salts of the alkalies—sodium and potassium. The following illustrates the similarity.

$NH_3 + HCl$	$=$	NH_4Cl Ammonium chloride.	$KCl.$ Potassium chloride.
$2NH_3 + H_2SO_4$	$=$	$(NH_4)_2SO_4$ Ammonium sulphate.	$K_2SO_4.$ Potassium sulphate.
$NH_3 + H_2S$	$=$	NH_4SH Ammonium sulphydrate.	$KSH.$ Potassium sulphydrate.

In these ammonia derivatives NH_4 plays the rôle of a metal. Hence, to show its similarity to sodium, potassium and other metals, the group (NH_4) has been designated *ammonium* and its compounds, *ammonium salts*. The latter, when acted on by strong bases, yield ammonia gas:

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O.$$

The metallic character of the ammonium group is also confirmed by the existence of the ammonium amalgam. Therefore, the ammonium derivatives will be considered with the metals.

Thermo-chemical Deportment.—The heat of formation of ammonia from hydrogen and nitrogen equals 12 Cal. When ammonia gas is dissolved in much water 8.4 Cal. are set free, so that the heat of formation of ammonia from its elements in dilute aqueous solution equals 20.4 Cal.:

$$(N,H_3 - \text{gas}) = 12. \quad (NH_3,Aq) = 8.4. \quad (N,H_3,Aq) = 20.4.$$

The great heat of solution of gaseous ammonia explains why ice will melt in the same (p. 127).

The explosibility of a mixture of ammonia and oxygen is accounted for by the following great heat disengagement:

$$\underset{(24\text{ Cal.})}{2NH_3} + 3O = \underset{(3 \times 57.2\text{ Cal.})}{3H_2O} + N_2 \quad . \; . \; (+ 147.6\text{ Cal.})$$

The action of chlorine upon gaseous or aqueous ammonia is also very energetic:

$$\underset{(12\text{ Cal.})}{NH_3\text{ gas}} + 3Cl = \underset{(66\text{ Cal.})}{3HCl\text{ gas}} + N \quad . \; . \; . \; (+ 54\text{ Cal.})$$

$$\underset{(20.4\text{ Cal.})}{NH_3\text{-dissolved}} + 3Cl = \underset{(3 \times 39.3\text{ Cal.})}{3HCl\text{-dissolved}} + N \quad . \; . \; . \; (+ 97.5\text{ Cal.})$$

When there is an excess of ammonia the hydrochloric acid combines with it to form ammonium chloride ($NH_3 + HCl = NH_4Cl$), and the heat disengagement is thereby further increased.

QUANTITATIVE COMPOSITION OF AMMONIA. ATOMIC WEIGHT OF NITROGEN.

The quantitative analysis of ammonia shows that it consists of 1.01 parts of hydrogen and 4.68 parts of nitrogen; hence we conclude that the atomic weight of nitrogen is 4.68 or a multiple of it (see p. 69):

$$\begin{array}{rcl@{\qquad}rcl@{\qquad}rcl}
H & = & 1 & 2H & = & 2.02 & 3H & = & 3.03 \\
N & = & 4.68 & N & = & 9.34 & N & = & 14.04 \\
\hline
NH & = & 5.68 & NH_2 & = & 11.36 & NH_3 & = & 17.07
\end{array}$$

As the density of ammonia equals 17.07 ($O_2 = 32$), its molecular weight would equal 17.07. In 17.07 parts of ammonia there are 3.03 parts, and, therefore, three atoms of hydrogen. That the 14.04 parts of nitrogen united with them correspond to *one* atom of nitrogen is a consequence, *as never less than 14.04 parts of that element are present in the molecular weight of any nitrogen derivative.* The density of nitrogen equals 28.08 ($O_2 = 32$); therefore, the molecule of nitrogen consists of two atoms (N_2). This is also concluded from the volume ratios, as we shall soon see, occurring in the decomposition of ammonia (compare p. 76).

From the molecular formulas NH_3 and N_2 it follows, further, that 1 volume of nitrogen and 3 volumes of hydrogen form 2 volumes of ammonia gas, or that 2 volumes of ammonia decompose into 3 volumes of hydrogen and 1 volume of nitrogen, corresponding to the molecular equation:

$$\underset{\text{1 vol.}}{N_2} + \underset{\text{3 vols.}}{3H_2} = \underset{\text{2 vols.}}{2NH_3}.$$

The following experiments prove these conclusions:

1. Decompose an aqueous ammonia solution, mixed with salt (NaCl) to increase its power of conductivity, in a Hofmann's apparatus (p. 77), by the galvanic current. Hydrogen will separate at the negative and nitrogen at the positive pole; the former will have three times the volume of the latter as soon as the solution is saturated with gases.

2. Pass electric (induction) sparks through dry ammonia gas contained in a eudiometer, or the apparatus represented in Fig. 47 (p. 98). In this way the ammonia is decomposed into nitrogen and hydrogen, the volume of which is twice as large as that of the ammonia employed. That 3 volumes of hydrogen are present in the mixture for every volume of nitrogen is easily shown by the eudiometric method, by burning the hydrogen with oxygen (p. 99).

2. HYDROXYLAMINE (OXYAMMONIA).

$NH_3O = NH_2OH.$

This compound was discovered (by Lossen in 1865), in the reduction of ethyl nitrate by tin and hydrochloric acid, in the form of its salts and in aqueous solution. Lobry de Bruyn first obtained it anhydrous and in a solid form in 1891. It is produced, too, by the action of tin upon dilute nitric acid, and by tin and hydrochloric acid upon all the oxygen compounds of nitrogen. In all these reactions it is the hydrogen eliminated by the tin which, *in statu nascendi*, reduces the nitric acid:

$$HNO_3 + 3H_2 = NH_3O + 2H_2O.$$

To prepare hydroxylamine treat ethyl nitrate (120 grams) with granulated tin (400 grams) and hydrochloric acid (800–1000 c.c. of specific gravity 1.19, mixed with three times its volume of water). The metal should be completely dissolved. The solution diluted to twice its volume is treated with hydrogen sulphide to precipitate the tin. The filtrate from the tin sulphide is evaporated and the hydroxylamine hydrochloride, $NH_3O . HCl$, extracted from the residue with hot alcohol.

Hydroxylamine hydrochloride is most easily formed by the interaction of hydrochloric acid and fulminating mercury (see Organic Chemistry).

Hydroxylamine sulphate is technically prepared by heating potassium hydroxylamine-disulphonate with water to 100–130°, when hydroxylamine sulphate and potassium sulphate are produced [see Raschig, Ann. Chem. 241 (1887), 161]:

$$NHO(SO_3K)_2 + 2H_2O = NH_3O \, . \, H_2SO_4 + K_2SO_4.$$

Potassium hydroxylamine-disulphonate is formed by the interaction of potassium nitrite and acid potassium sulphite in the cold:

$$KNO_2 + 2KHSO_3 = NHO(SO_3K)_2 + KOH.$$

To obtain *solid hydroxylamine* decompose the hydrochloride in methyl alcohol solution by a corresponding quantity of sodium methylate; filter from the sodium chloride which separates and distil the filtrate under greatly reduced pressure [Brühl, Ber. 26 (1893), III, 2508; also Lobry de Bruyn, *ibid.* 27 (1894), I, 967].

Hydroxylamine crystallizes in colorless, odorless needles. It melts at 33° and under 22 mm. pressure boils at 58°. Its specific gravity equals 1.235. It is rather stable at temperatures below 15°, but above that it rapidly breaks down into nitrogen, nitrous oxide, nitrous acid and ammonia. At about 130° and often at much lower temperatures the decomposition is accompanied with explosion. It absorbs moisture rapidly on exposure to the air.

Hydroxylamine is very similar to ammonia, and like it unites directly with the acids to form salts:

$$NH_3O + HCl = NH_3O \, . \, HCl = NH_3(OH)Cl.$$

Hydroxylamine hydrochloride in distinction to ammonium chloride is soluble in alcohol. It passes into ammonium chloride when allowed to stand exposed to the air.

On adding to the aqueous solution of the sulphate of hydroxylamine sufficient barium hydroxide to remove all the sulphuric acid, an aqueous solution of hydroxylamine is obtained, which, like the ammonia solution, possesses strong basic properties, and colors red litmus-paper blue. The solution is, however, very unstable, and readily decomposes into water, ammonia, and nitrogen:

$$3NH_3O = NH_3 + 3H_2O + N_2.$$

Upon the application of heat a portion of the hydroxylamine will be carried over undecomposed along with the steam, but most of it is decomposed. The hydroxylamine solution manifests a strong reducing action; it precipitates metallic silver from silver nitrate, white mercurous chloride, Hg_2Cl_2, from mercuric chloride, $HgCl_2$, and cuprous oxide from cupric salts.

Owing to its great similarity to ammonia and its various reactions, it is supposed that hydroxylamine represents ammonia in which an hydrogen atom is replaced by the hydroxyl group OH; it is therefore a compound of the latter group with the amido group:

$$NH_3O = NH_2 \, . \, OH.$$

3. **Diamide, or Hydrazine,** $N_2H_4 = H_2N \, . \, NH_2$, a compound of two amido-groups (NH_2), was until 1889 only known in its numerous organic derivatives. Since then Curtius and his co-workers have exhaustively investigated a large number of its inorganic compounds, and in 1895 Lobry de Bruyn succeeded in getting the free diamide or hydra-

zine unknown until then [Ber. 28 (1895), 3085]. Its salts were first made by an indirect method from certain organic nitrogen derivatives: by the decomposition of diazo- or triazo-acetic acid upon digesting them with water or mineral acids [Curtius and Jay, J. f. prakt. Ch. [2] 39 (1889), 27]; by heating amidoguanidine with sodium hydroxide [Thiele, Ann. Chem. 270 (1892), 31], etc. See also the last edition of Richter's Organic Chemistry. Very recently diamide has been made from inorganic compounds: by the reduction of nitric oxide-potassium sulphite with nascent hydrogen:

$$K_2SO_3 . N_2O_2 + 3H_2 = N_2H_4 . H_2O + K_2SO_4$$

[Duden, Ber. 27 (1894), 3498].

Free hydrazine, like free hydroxylamine, is prepared by decomposing its hydrochloride with sodium methylate:

$$N_2H_4 . HCl + CH_3ONa = NaCl + CH_3OH + N_2H_4.$$

It may also be obtained by distilling its hydrate under reduced pressure with barium oxide. It is a colorless liquid, fuming strongly in the air, boiling at 113.5° and solidifying at 0°. It melts at 1.4°. Its specific gravity is about 1.003 at 23°. It is not explosive and is stable even at 300°. Its hydrate, $N_2H_4 . H_2O$, is a strong base, very much like ammonia. It is produced when the hydrazine salts are decomposed by powerful bases. It is characterized by great reducing power. It will be discussed later along with the diammonium salts in concluding the alkaline earth metals.

4. **Hydrazoic Acid, or Azoïmide,** $N_3H =$  $\left.\begin{matrix}N\\ \| \\ N\end{matrix}\right\rangle NH$, was also discovered by Curtius in 1890 [Ber. 23 (1890), 3023]. It was, like the preceding body, first isolated from organic derivatives, and indeed from those of diamide [especially benzoyl azoïmide which upon digestion with sodium alcoholate yields sodium azoïmide and ethyl benzoate:

$$C_6H_5CON_3 + C_2H_5ONa = NaN_3 + C_6H_5COOC_2H_5,$$

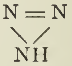
and from diazohippuramide which is resolved by ammonia into ammonium azoïmide, hippuramide and ammonia:

$$C_6H_5CO\text{–}NH\text{–}CH_2\text{–}CO\text{–}NH\text{–}N{=}N\text{–}OH + 2NH_3 =$$
$$N_3 . NH_4 + H_2O + C_6H_5CO\text{–}NH\text{–}CH_2\text{–}CO\text{–}NH_2.$$

[A description of these investigations can be found in the Jahrbuch der Chemie I (1891), 91, 227; II (1892), 229; also Thiele, Ann. Chem. 270 (1892), 53, and Richter's Organic Chemistry.]

The following are real inorganic methods for the preparation of hydrazoic acid or its salts.

Curtius prepares a dilute aqueous solution of the acid by chilling with ice the red vapors arising from heating arsenious oxide and nitric acid (see Nitrous Acid) and adding the resulting blue liquid gradually, as long as gas is not evolved, to a cold solution of hydrazine. This is analogous to the formation of silver azoïmide (Angeli) from silver nitrite and hydrazine sulphate:



$$H_2\text{–}N\text{–}NH_2 + NO_2H = H_2\text{–}N\text{–}N{=}N\text{–}OH + H_2O = \begin{matrix}N = N\\ \diagdown\ \diagup\\ NH\end{matrix} + 2H_2O.$$

Wislicenus asserts that sodium azoïmide is readily obtained by heating sodamide to 150–240° in a current of nitrous oxide:

$$NH_2Na + N_2O = NaN_3 + H_2O.$$

Dilute aqueous solutions of hydrazoic acid may be obtained by distilling the metallic azoïmides with dilute sulphuric acid. By further distillation of the solution and by means of calcium chloride the acid may be obtained anhydrous when it is a colorless, mobile liquid with an unbearable odor. It boils at 37°, volatilizes with steam, and is characterized by its exceptionally violent explosibility. In this respect it differs from the haloid acids, especially hydrochloric acid, with which it possesses many points of similarity. This behavior would indicate that hydrazoic acid is a strongly endothermic body:

$$(N_3,H) \text{ dissolved} = -62 \text{ Cal.}$$

Its alkali salts are not explosive. Some of the alkaline earth salts explode when heated, and some of the heavy metals when touched or struck. These salts will be further treated under the respective metals. [See Curtius and Rissom, Jr. prakt. Ch. **58** (1898), 261; also Z. f. anorg. Ch. **17** (1898), 18.]

COMPOUNDS OF NITROGEN WITH THE HALOGENS.

NITROGEN CHLORIDE.

NCl_3.

As we have seen, nitrogen is liberated when chlorine acts upon an excess of ammonia (p. 116); when, however, the chlorine is in excess, it acts upon the previously formed ammonium chloride to produce nitrogen chloride:

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl.$$

For the preparation of a small quantity of nitrogen chloride, dip a flask filled with chlorine, open end down, into an aqueous ammonium chloride solution warmed to 30°. The chlorine is absorbed, and heavy oil drops separate, which are best collected in a small leaden dish. They contain hydrogen in addition to nitrogen and chlorine. They yield pure nitrogen chloride by a second treatment with chlorine [see Gattermann, Ber. **21** (1888), 751]. A pentachloride of nitrogen, NCl_5, is not known.

Nitrogen chloride is an oily, yellow liquid, with a disagreeable odor; its specific gravity equals 1.65. It does not solidify even at —40°. It is an extremely dangerous compound, as it decomposes by the slightest contact with many substances, when the temperature exceeds 90° and by the action of direct sunlight. Its decomposition is accompanied by an extremely violent report. Its solution in benzene, ether and carbon bisulphide can be handled with comparatively little danger; but it rapidly decomposes in them. Aqueous ammonia gradually decomposes it into ammonium chloride and nitrogen:

$$NCl_3 + 4NH_3 = 3NH_4Cl + N_2.$$

It is converted into ammonium chloride and free chlorine by concentrated hydrochloric acid:

$$NCl_3 + 4HCl = NH_4Cl + 3Cl_2.$$

This reaction is directly opposed to that by which nitrogen chloride is formed.

Nitrogen chloride is decomposed by water partly into hypochlorous acid [see Ber. 27 (1894), I, 1017, and 30 (1897), II, 1434, 1792; III, 2642].

The formation and explosibility of nitrogen chloride may be illustrated in a harmless way as follows: Decompose a saturated ammonium chloride solution with the electric current. Nitrogen chloride rising in small drops from the liquid will separate at the positive pole. Upon covering the surface of the solution with a thin layer of turpentine oil, each drop will explode as it comes in contact with the latter.

Nitrogen Iodide. Upon adding ammonium hydroxide, or a mixture of ammonium chloride and caustic soda, to a solution of iodine in aqueous potassium iodide, a brownish-black powder separates. Its composition closely approximates the formula, NHI_2. Its formation by means of ammonium chloride and caustic soda is represented in the equation:

$$4I + NH_4Cl + 3NaOH = NHI_2 + 3H_2O + NaCl + 2NaI.$$

[Compare Raschig, Ann. Chem. 230 (1885), 212.]

When the conditions are slightly changed a very similar compound separates. Its formula is $N_2I_3H_3 (= NH_3 + NI_3)$. Protracted washing with water decomposes it into ammonia and nitrogen tri-iodide, NI_3.

Nitrogen Di-iodide and **Nitrogen Tri-iodide**, NHI_2 and NI_3, are, when dry, very explosive. The explosibility may be shown without danger in the following manner: The precipitate is collected on a filter, washed with water, the filter opened out and torn into small pieces, which are then allowed to dry; upon the slightest disturbance these pieces explode with a sharp report.

Szuhay claims that nitrogen iodide, NHI_2, behaves like a feeble acid and that its silver salt, $NAgI_2$, explodes [Ber. 26 (1893), II, 1933].

Nitrogen iodide dissolves in dilute hydrochloric acid and decomposes into ammonia and iodine monochloride:

$$NH_2I + HCl = NH_3 + ICl.$$

Hydrogen sulphide and sulphurous acid convert it into ammonia and hydrogen iodide.

The nitrogen iodide formed by digesting powdered iodine with ammonia water manifests properties which are slightly different from those of the ordinary iodide. It is only stable in the presence of ammonia. It sometimes explodes even when moist—if it be washed with water, or when acted upon by hydrochloric acid.

Thermo-chemical Deportment.—Nitrogen chloride and iodide are both strongly endothermic compounds; considerable heat is absorbed in their production from the elements. This again presupposes conditions under which the nitrogen halides would be no longer stable. Consequently their heat of formations cannot be obtained by direct measurement but must be calculated from other thermo-chemical relations. That for nitrogen chloride is

$$(N,Cl_3) = -41.9 \text{ Cal.}$$

2. PHOSPHORUS.

Atom: $P = 31.0$. Molecule: $P_4 = 124.0$.

This element does not occur free in nature, because of its very great affinity for oxygen. The phosphates, especially calcium phosphate, are widely distributed. By the disintegration of the minerals containing phosphates the latter pass into the soil, are absorbed by plants, and these are consumed by animals. Hence phosphates occur in both plant and animal ashes. The bones of animals consist chiefly of calcium phosphate.

Brand, in Hamburg, and Kunkel, in Wittenberg (1670), obtained phosphorus almost simultaneously by the ignition of evaporated urine. In 1755, Scheele, in Sweden, showed that it could be obtained from bones, in which Gahn had found calcium phosphate. Its name is derived from its power of giving light in the dark—*φωσφόρος*, light-bearer.

Phosphorus is prepared in France and in England almost exclusively in accordance with a method first suggested in 1778 by Nicolas and Pelletier, which method was subsequently improved by Fourcroy and Vauquelin.

The bones are burned, thereby destroying all organic admixtures, or they are first treated with superheated steam to remove the bone glue. The bone ashes consist principally of tertiary calcium phosphate $Ca_3(PO_4)_2$ (see Phosphoric Acid). They are digested with two-thirds of their weight of concentrated sulphuric acid, when the tertiary phosphate becomes primary calcium phosphate, and gypsum (calcium sulphate) is produced:

$$\underset{\substack{\text{Tertiary}\\\text{calcium phosphate.}}}{Ca_3(PO_4)_2} + 2H_2SO_4 = \underset{\substack{\text{Primary}\\\text{calcium phosphate.}}}{CaH_4(PO_4)_2} + \underset{\substack{\text{Calcium}\\\text{sulphate.}}}{2CaSO_4.}$$

The gypsum, which dissolves with difficulty in water, is separated from the readily soluble primary phosphate by filtration; the solution is mixed with charcoal, evaporated in leaden pans, and the residue raised to a red heat in clay retorts. This expels water from the primary phosphate and the latter changes to calcium metaphosphate:

$$CaH_4(PO_4)_2 = \underset{\substack{\text{Calcium}\\\text{metaphosphate.}}}{Ca(PO_3)_2} + 2H_2O.$$

The ignited residue is then raised to a white heat. The carbon partly reduces the metaphosphate to phosphorus, by forming carbon monoxide with oxygen. The resulting calcium oxide in like manner converts a portion of the metaphosphate into tertiary phosphate, which is not further attacked by the carbon. The following equations show the changes:

$$\begin{array}{rl}
\text{I.} & 2Ca(PO_3)_2 + 10C = P_4 + 10CO + 2CaO \\
\text{II.} & Ca(PO_3)_2 + 2CaO = Ca_3(PO_4)_2 \\
\hline
 & 3Ca(PO_3)_2 + 10C = P_4 + Ca_3(PO_4)_2 + 10CO.
\end{array}$$

Recently the great heat of the electric furnace has been applied in carrying out a method suggested by Wöhler, but which has not until the present been made operative: the tertiary phosphate, mixed with sand, is reduced by carbon. The silicic acid (sand) acts like the sulphuric acid, in that it liberates phosphoric acid when heated:

$$2Ca_3(PO_4)_2 + 10C + 6SiO_2 = 6CaSiO_3 + 10CO + 4P.$$

Mineral phosphates have been worked for phosphorus in a similar way.

The liberated phosphorus escapes in vapor form, and is collected and condensed under water in receivers of peculiar construction. To remove mechanically admixed impurities the phosphorus is again distilled from retorts, melted under water, pressed through leather or chamois, or through bone ash, and finally moulded into sticks.

Phosphorus may be obtained by the method of Rossel on a small scale, if 2.5 parts of aluminium powder, 6 parts of sodium metaphosphate, and 2 parts of silica are carefully heated in a glass tube in a current of hydrogen:

$$6NaPO_3 + 10Al + 3SiO_2 = 3Na_2SiO_3 + 5Al_2O_3 + 6P.$$

(Compare Chemiker-Zeitung, 1898, 237.)

The almost colorless phosphorus obtained by distillation is a waxy, transparent substance, of specific gravity 1.83 at 10° C. At ordinary temperatures it is soft and tough; at 0° it becomes brittle. It fuses under water at 44.4° and boils at 287°. By the action of sunlight it becomes yellow (hence called *yellow phosphorus*), and is coated with a non-transparent, reddish-white layer. Phosphorus is insoluble in water, slightly soluble in alcohol and ether, and very readily soluble in carbon bisulphide. It crystallizes from the latter solution in forms of the isometric system (rhombic dodecahedra). When exposed to moist air, it oxidizes to phosphorous acid (H_3PO_3) and phosphoric acid (H_3PO_4); the white vapors which arise contain ammonium nitrite (NH_4NO_2), ozone, and hydrogen peroxide. The odor of phosphorus resembles that of ozone. It phosphoresces in the dark on exposure to air. It does this also in other gases, but only in such as contain oxygen. It appears the phosphorescence is influenced by the formation and combustion of the self-inflammable phosphine, as all substances which destroy the latter prevent and put an end to the former. It is noteworthy that in pure oxygen the oxidation of phosphorus begins at 27°. If the oxygen be diluted by removal over an air pump or by the addition of neutral gases, so that its quantity is not more than 40 per cent., the absorption will be very energetic at 20°, but cease entirely at 7°.

The *red phosphorus*—discovered by v. Schrötter in 1845—possesses properties entirely different from those of the ordinary variety. It is a reddish-brown powder, of specific gravity 2.19; is not amorphous as formerly believed but, according to the investigations of Retgers, it is hexagonal (Z. f. anorg. Chem. v (1894), 211). It is insoluble in carbon bisulphide, non-phosphorescent, does not alter in the air, and is, indeed, very stable. While ordinary phosphorus is very poisonous, the red variety is perfectly harmless. It does not fuse at a red heat, even when subjected to strong pressure, and vaporizes very slowly (even at 100°), without changing to the yellow variety; but when it is heated rapidly (above 260°) the vapors change to those of yellow phosphorus.

To prepare the red variety, yellow phosphorus is heated for some minutes to 300°, in closed, air-tight iron vessels; there is a partial conversion at 250°. The resulting mass is then treated with carbon bisulphide or sodium hydroxide, to withdraw the unaltered, ordinary phosphorus. If iodine be added to the ordinary phosphorus, the change will occur below 200°.

A third modification—*metallic phosphorus*—is formed if the amorphous variety be heated in a glass tube, free from air, to 530°. Microscopic needles then sublime into the upper, less heated, portion of the tube. It is more easily obtained if phosphorus is heated with lead, in a closed tube, to a red heat. The molten metal dissolves the phosphorus and, on cooling, the latter separates in black, metallic, shining crystals (Hittorf). Metallic phosphorus possesses the specific gravity 2.34, vaporizes with difficulty, and is less active than the red variety. Perhaps it consists of a better crystallized form of the red variety.

Two green lines characterize the spectrum of phosphorus. On conducting hydrogen over a small piece of phosphorus, heated in a glass tube, the escaping gas will burn with a bright green flame. When ordinary phosphorus is distilled with water, some passes over with the steam and, in the dark, phosphoresces. This procedure serves for the detection of phosphorus in poisoning by this substance (Mitscherlich).

The density of phosphorus is referred to $O_2 = 32$ and therefore its molecular weight is 124. As the atomic weight of phosphorus is 31.0, it follows that the molecule in the form of vapor consists of 4 atoms: $P_4 = 124.0$. We saw that the sulphur molecule at 500° consists of 6 atoms (S_6), and at 900° of 2 atoms (S_2). Such a dissociation does not, however, occur with phosphorus; even at 1040° its vapor density remains unaltered, although a partial dissociation does take place at a very intense heat.

When phosphorus is burned in oxygen or in air, it forms the pentoxide (P_2O_5). The ordinary variety inflames at 40°, and also by gentle friction; the red is not ignited below 260°. The first will burn with a bright flame even under water. To this end heat pieces of phosphorus in a flask with water, until they melt, and conduct a current of oxygen through the water. Phosphorus combines very energetically with chlorine, bromine, and iodine at ordinary temperatures; on throwing a small piece into a vessel containing dry chlorine gas it at once inflames. The red only reacts with the halogens after applying heat. With most of the metals phosphorus unites on warming, and precipitates some of them from solutions of their salts. From a silver nitrate solution, it precipitates silver and silver phosphide (Ag_3P); this solution, therefore, answers as a counterirritant in phosphorus burns.

The difference in deportment of the yellow and the red phosphorus is fully accounted for by the circumstance, that when the red is produced from the yellow there follows a considerable heat-disengagement:

$$\text{P yellow} = \text{P red} + 19.2 \text{ Cal.}$$

Hence, the red variety contains much less energy than the yellow. In its union with other substances there will always be liberated 19.2 Cal. less, and the reaction consequently will proceed more sluggishly and with less energy. It may be assumed, that in the yellow phosphorus, owing to the very energetic motions of its atoms their mutual affinity acts in a much reduced form; the atoms are loosely combined with one another and are therefore very reactive. In the passage of the yellow into the red or black variety the energy of the atom motions is converted into thermal energy, and the atoms can attach themselves more firmly to one another than before, the molecule is more stable, the reactivity is diminished. Formerly when heat was still regarded as a substance, such relations as those above were well expressed by the terms *calorous*—bodies containing but little heat, and *calorids*—bodies rich in heat.

COMPOUNDS OF PHOSPHORUS WITH HYDROGEN.

PH_3, P_2H_4, P_4H_2.

The compounds of phosphorus with hydrogen can be prepared by the action of nascent hydrogen upon phosphorus, as, for example, on gently heating dilute sulphuric acid with zinc and phosphorus (compare p. 144). The usual course is to heat yellow phosphorus with concentrated potassium or sodium hydroxide, when spontaneously inflammable phosphine escapes and a salt of hypophosphorous acid remains in solution.

The liberated gas mixed with air in a closed vessel explodes violently; hence, to make it, proceed as follows: Fill a small glass flask almost full of aqueous potassium hydroxide, add a few pieces of phosphorus, and heat over a lamp (Fig. 55). When the liberation of gas commences, and the air in the neck of the flask has been expelled, close the same with the cork of the delivery tube, the other end of which dips under *warm* water, to prevent any obstruction arising in it from phosphorus that may be carried over and solidify by cooling. Each bubble rising from the liquid inflames in the air, and forms white cloud-rings which ascend.

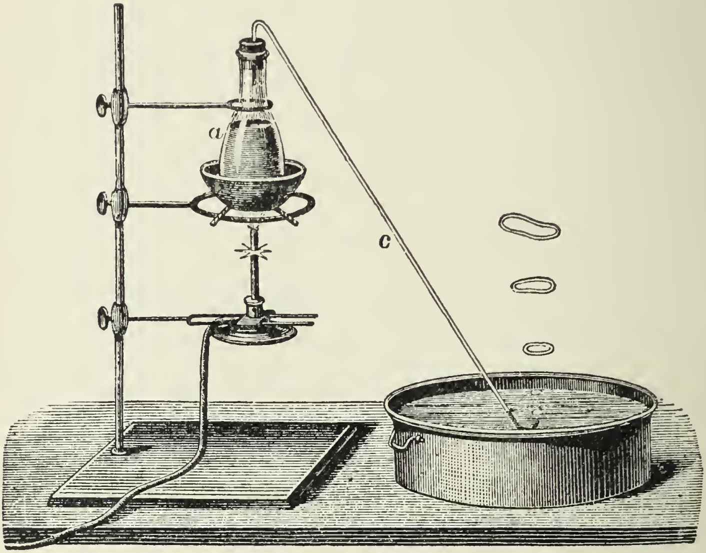


FIG. 55.

The gas thus produced consists of gaseous phosphine (PH_3) and hydrogen, with which is mixed a small quantity of a liquid substance (P_2H_4), whose presence imparts the spontaneous inflammability to the gas. On conducting the latter through a cooled tube the P_2H_4 is condensed to a liquid, and the escaping gas no longer inflames spontaneously. The liquid compound may be isolated in a similar manner if the gas is conducted through alcohol or ether, which will absorb the compound P_2H_4.

Liquid Phosphine, P_2H_4, separated from the gas by cooling, is a colorless, strongly refracting liquid of specific gravity 1.012, insoluble in water, and boiling at 57° [Gattermann and Hausknecht, Ber. 23 (1890), 1174]. It inflames spontaneously in the air, and burns with great brilliancy to phosphorus pentoxide and water. Its presence in combustible gases, such as hydrogen, marsh gas, and gaseous phosphine, gives them their spontaneous inflammability. In contact with some compounds, like carbon and sulphur, and by the action of sunlight and of strong hydrochloric acid, it decomposes into gaseous and solid phosphine:

$$5P_2H_4 = 6PH_3 + P_4H_2.$$

Solid Phosphine, P_4H_2 (?) is a yellow powder, which inflames at 160° or by a blow. It is produced in the decomposition of calcium phosphide by hydrochloric acid.

Gaseous Phosphine, PH_3, may be formed, together with the liquid and solid variety, in addition to the manner previously described, by the action of water or hydrochloric acid upon the calcium phosphides, Ca_3P_2 and Ca_2P_2:

$$\begin{aligned} Ca_3P_2 + 6HCl &= 3CaCl_2 + 2PH_3; \\ Ca_2P_2 + 4HCl &= 2CaCl_2 + P_2H_4; \\ 5P_2H_4 &= 6PH_3 + P_4H_2. \end{aligned}$$

Further, by the ignition of phosphorous and hypophosphorous acids:

$$\underset{\text{Phosphorous acid.}}{4H_3PO_3} = PH_3 + \underset{\text{Phosphoric acid.}}{3H_3PO_4}$$

and by decomposing phosphonium iodide with caustic potash (p. 140).

It is a colorless gas, with a disagreeable, garlic-like odor, and is slightly soluble in alcohol. Its density is 34.03 referred to $O_2 = 32$, or 1.176 (air = 1). It solidifies at —133.5° and boils at about —85°. When pure (free from P_2H_4) it ignites at 100°. Oxidizing agents convert it again into the spontaneously inflammable variety, owing to the production of P_2H_4. It is extremely poisonous. Phosphine is decomposed into phosphorus and hydrogen when it is heated, or if it is exposed to the action of the electric spark. When ignited in the air it burns with a brightly luminous flame, disseminating at the same time a white cloud of phosphorus pentoxide (P_2O_5):

$$2PH_3 + 4O_2 = 3H_2O + P_2O_5.$$

When mixed with chlorine it explodes violently, with production of phosphorus trichloride and hydrogen chloride:

$$PH_3 + 3Cl_2 = PCl_3 + 3HCl.$$

Like ammonia, phosphine possesses faint alkaline properties, and combines with hydrogen iodide and bromide to yield compounds similar to ammonium chloride:

$$PH_3 + HI = PH_4I.$$

It combines with hydrogen chloride at from —30° to —35°, or, at ordinary temperatures, under a pressure of 20 atmospheres. The group PH_4, figuring in the rôle of a metal in these compounds, is analogous to ammonium (p. 129), and is termed *phosphonium*.

Phosphonium Iodide, PH_4I. It is best prepared by the decomposition of phosphorus di-iodide (P_2I_4, p. 142), by a slight quantity of water, or by adding yellow phosphorus (10 parts), and, after some hours, iodine (2 parts), to a saturated solution of hydriodic acid (22 parts). The liquid becomes a solid mass, consisting of phosphonium iodide and phosphorous acid. Phosphonium iodide sublimes in colorless, shining, cube-like rhombohedra and by this means may be obtained pure. It fumes in the air, and, with water, decomposes into phosphine and hydrogen iodide. When decomposed by potassium hydroxide it yields pure hydrogen phosphide, which is not spontaneously inflammable:

$$PH_4I + KOH = KI + PH_3 + H_2O.$$

Phosphine is a feebly exothermic compound:

$$P \text{ yellow} + 3H = PH_3 + 11.6 \text{ Cal.}$$

MOLECULAR FORMULA OF PHOSPHINE. ATOMIC WEIGHT OF PHOSPHORUS.

The analysis of phosphine shows that it consists of 1.01 parts of hydrogen and 10.33 parts of phosphorus. Were its molecular formula PH, the atomic weight of phosphorus would be 10.33. The great analogy of phosphine to ammonia, and that of all the phosphorus compounds to those of nitrogen, argues, however, for the formula PH_3. The atomic weight of phosphorus, therefore, is 31.00 ($= 3 \times 10.33$), and the molecular weight of the phosphine is 34.03:

$$\begin{array}{rl} H_3 = & 3.03 \\ P = & 31.00 \\ \hline PH_3 = & 34.03 \end{array}$$

This view is confirmed by the density. Direct experiment confirms this. Further, from the formula PH_3 it follows that 3 volumes of hydrogen are present in 2 volumes of the gas:

$$\underset{\text{2 vols.}}{2PH_3} \quad \text{contain} \quad \underset{\text{3 vols.}}{3H_2},$$

or in 1 volume there are 1½ volumes of hydrogen. On decomposing the gas in a eudiometer, by means of electric sparks, it will be found that the volume increases one-half; the gas consists, then, of pure hydrogen, while phosphorus separates in a solid condition. As the phosphorus molecule in the gaseous condition is composed of four atoms (p. 137), the phosphorus (62.00 parts) separated from 2 volumes of phosphine will fill ½ volume when in the form of vapor; hence in 2 volumes of phosphine there are present 3 volumes of hydrogen and ½ volume of phosphorus vapor.

Or, written molecularly:

$$\underset{\text{1 vol.}}{4PH_3} = \underset{\text{1 vol.}}{P_4} + \underset{\text{6 vols.}}{6H_2}.$$

COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS.

Phosphorus combines directly with the halogens to yield compounds of the types PX_3 and PX_5, in which X indicates an halogen atom.

Phosphorus Trichloride—*Phosphorous Chloride*—PCl_3. Conduct dry chlorine gas over phosphorus gently heated in the retort *C* (Fig. 49, p. 111). The phosphorus ignites in the stream of gas, and distils over as trichloride, which is collected in the receiver *D*, and condensed. The product is purified by a second distillation. It is a colorless liquid, congealing at —112°, boiling at 76°, and has a sharp, penetrating odor. Its specific gravity equals 1.613 at 0°. It fumes strongly in the air, and is decomposed by moisture into phosphorous and hydrochloric acids:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

The vapor density of the trichloride is 137.35, corresponding to the molecular formula PCl_3.

Phosphorus Pentachloride—*Phosphoric Chloride*—PCl_5. This is produced by the action of an excess of chlorine upon the liquid trichloride. It is a solid, crystalline, yellowish-white compound. It fumes strongly in the air and sublimes without melting when heated. It at the same time sustains a partial decomposition into trichloride and chlorine. Under increased pressure it melts at 148°.

In an atmosphere of phosphorus trichloride the vapor density of the pentachloride has been found to be 208.25, corresponding to the molecular formula $PCl_5 = 208.25$. At increased temperatures the vapor density steadily diminishes, and a gradual decomposition occurs—dissociation of the molecules of the pentachloride (PCl_5) into the molecules of the trichloride (PCl_3), and chlorine (Cl_2). The decomposition temperature, *i. e.*, the temperature at which the decomposition is half finished, lies at about 200° C. The dissociation is complete at 300°, and equals 104, the vapor density; *i. e.*, the vapor then fills a volume twice as large as at a lower temperature. The breaking down of the pentachloride into the trichloride and chlorine, whereby $2n$ molecules result from n molecules, explains this:

$$\underset{\text{1 vol.}}{PCl_5} = \underset{\text{1 vol.}}{PCl_3} + \underset{\text{1 vol.}}{Cl_2}.$$

That such a decomposition of the penta- into trichloride and chlorine does really occur, is proved, among other things, by the originally colorless vapor gradually assuming the yellow color of chlorine as the temperature rises. The decomposition products—the trichloride and chlorine—may be separated from each other by diffusion.

Phosphorus pentachloride acts very energetically with water; it yields, depending upon the quantities of the reacting substances, phosphorus oxychloride, $POCl_3$, metaphosphoric acid, HPO_3, or orthophosphoric acid, H_3PO_4, and hydrochloric acid:

$$PCl_5 + H_2O = POCl_3 + 2HCl$$
$$PCl_5 + 3H_2O = HPO_3 + 5HCl$$
$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl.$$

(See Phosphoric Acid.)

The bromine and iodine phosphorus compounds are perfectly analogous to the chlorine derivatives. They are obtained by uniting the constituents in the proportions by weight expressed by their formulas. As the union is exceedingly energetic, it is best to proceed as follows: Dissolve the phosphorus in carbon bisulphide, gradually add the calculated amount of bromine or iodine, and then distil off the volatile solvent.

Phosphorus Tribromide, PBr_3, is a colorless liquid, boiling at 175°, and having a specific gravity of 2.9 at 0°. The **pentabromide**, PBr_5, formed by the gradual addition of 2Br to PBr_3, is a yellow, crystalline substance, which melts when heated, and breaks down into the tribromide and bromine. Water decomposes both compounds, as it does the corresponding chlorides.

Phosphorus Chlorbromide, PCl_3Br_2, is produced by the union of PCl_3 with Br_2 in the cold. It is a yellowish-red mass, which decomposes at 35° into PCl_3 and Br_2.

Phosphorus Tri-iodide, PI_3, forms red crystals, melting at 55° and distils, with partial decomposition, at a higher temperature. The so-called phosphorus iodide, P_2I_4 (corresponding to P_2H_4), crystallizes in beautiful orange-red needles or prisms, and fuses at 110°. Its vapor density at 265° and 90.7 mm. pressure equals 569, corresponding to the molecular weight P_2I_4. A little water decomposes it into phosphorous acid, phosphine, and hydriodic acid. The last two bodies then form *phosphonium iodide*, PH_4I (p. 140).

The recently discovered **Phosphorus Pentafluoride**, PFl_5, is interesting (Thorpe). It results upon heating phosphorus trichloride or pentachloride with arsenic trifluoride, $AsFl_3$:

$$3PCl_5 + 5AsFl_3 = 3PFl_5 + 5AsCl_3.$$

It is a colorless gas which fumes in moist air and is decomposed by water into phosphoric acid and hydrogen fluoride. Its density corresponds to the molecular formula $PFl_5 = 125.9$. It may be liquefied at 16° under a pressure of 46 atmospheres, and solidifies when the pressure is removed.

It is rather remarkable that although phosphorus pentiodide could not be obtained, the stability of the compounds, PBr_5, PCl_5, PFl_5, gradually increases with the diminution of the atomic weight of the combined halogens. Phosphorus pentafluoride can be gasified without decomposition.

Thermo-chemical Deportment.—While the halogen derivatives of nitrogen (like those of oxygen) are strongly endothermic, are produced with the absorption of much heat, and are, in consequence, readily exploded (p. 134), those of phosphorus are exothermic. The heat disengaged in the union of yellow phosphorus and chlorine (p. 137) corresponds to the following symbols:

$$(P,Cl_3) = 75.5\,;\ (P,Cl_5) = 105.$$

In this we observe a transition to the halogen derivatives of the metals, all of which are exothermic. In accordance with this we find that the heat of formation of the bromides and iodides diminishes in regular succession:

$$(P,Cl_3) = 75.5\,;\ (P,Br_3) = 45\,;\ (P,I_3) = 10.9.$$

The great reactivity of all these derivatives with water is fully explained by the large amount of heat set free at the same time—*e. g.*, the decomposition of phosphorus trichloride with so much water that upon diluting the resulting solution, no further heat evolution takes place:

$$PCl_3 + Aq = H_3PO_3Aq + 3HClAq \ . \ . \ . \ +65 \text{ Cal.}$$

3. ARSENIC.

Atom: As = 75. Molecule: As_4 = 300.

Arsenic is a perfect analogue of phosphorus, but possesses a somewhat metallic character. In its free state it is similar to metals.

Arsenic is found free in nature, although it occurs more frequently in combination with sulphur (realgar, As_2S_2, orpiment, As_2S_3), with oxygen (arsenolite, As_2O_3), and with metals (mispickel, FeAsS, cobaltite, CoAsS). To prepare it, heat mispickel with iron, and free arsenic will sublime, while iron sulphide remains. Or, in the customary way of isolating metals from their oxides, heat the trioxide (arsenolite) with charcoal:

$$2As_2O_3 + 6C = As_4 + 6CO.$$

Arsenic appears in two modifications. *Crystallized* (hexagonal) arsenic is obtained by the sublimation of ordinary arsenic. It forms a gray-white, more or less metallic, crystalline mass, but may be changed into acute rhombic octahedra. Its specific gravity equals 5.73. It is brittle, and may be pulverized without difficulty.

The *amorphous* variety is microcrystalline (according to Retgers) and probably *isometric*. It is formed along with the first variety when arsenic is sublimed in a glass tube in a current of hydrogen (Bettendorff) and also upon heating arsine. It is black, with little luster, and possesses the specific gravity 4.71. When heated to 360° it sets heat free and reverts to the crystalline variety.

Away from air contact, and at the ordinary pressure, arsenic vaporizes at a dark-red heat (about 450°) without previously melting; it will, however, melt if heated under great pressure in a sealed tube. Its vapor possesses a lemon-yellow color. The vapor density corresponds to the molecular weight. As its atomic weight equals 75, it follows that the molecule in the gaseous state consists, like that of phosphorus, of four atoms. At a white heat (about 1700°) the density falls to one-half, which is due to the fact that then the arsenic vapor consists largely of diatomic molecules ($As_2 = 150$).

Arsenic does not change in dry air. When heated in the air it inflames at 180° and burns with a blue-colored flame, disseminating the garlic-like odor of arsenic trioxide (As_2O_3). It combines directly with most elements. Powdered arsenic will inflame when thrown into chlorine gas. It yields arsenides with the metals.

It is remarkable that arsenic, belonging to the nitrogen group and generally forming compounds which in constitution are quite different from those of sulphur, should be analogous to the latter in its metallic combinations. Thus the sulphides and arsenides have similar formulas, are isomorphous, and in them sulphur and arsenic can mutually replace each other in atomic ratios, *e. g.*:

$$FeS_2,\ FeAs_2 \text{ and } Fe(SAs).$$

COMPOUNDS OF ARSENIC WITH HYDROGEN.

Arsine, $AsH_3 = 78.03$. Like nitrogen and phosphorus, arsenic furnishes a gaseous compound containing three atoms of hydrogen. It is obtained pure by the action of dilute sulphuric acid or hydrochloric acid upon an alloy of zinc and arsenic:

$$As_2Zn_3 + 6HCl = 3ZnCl_2 + 2AsH_3.$$

It also results in the action of nascent hydrogen (zinc and sulphuric acid), upon many arsenic compounds, as, *e. g.*, the trioxide:

$$As_2O_3 + 6H_2 = As_2H_3 + 3H_2O.$$

Arsine, discovered by Scheele in 1755, is a colorless gas, of strong, garlicky odor, and extremely poisonous action; it may be condensed to a liquid and even to a solid by cold. It melts at —113.5° and boils at —55°. Its density equals 78.03 ($O_2 = 32$) or 2.69 (air = 1). It burns with a bluish-white flame when ignited, and evolves white fumes of arsenic trioxide:

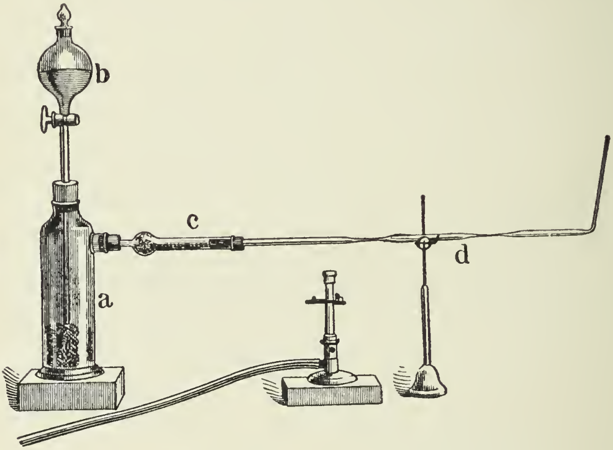


Fig. 56.

$$2AsH_3 + 3O_2 = As_2O_3 + 3H_2O.$$

It is decomposed at a dull-red heat or by the electric spark into arsenic and hydrogen. On conducting the gas through a heated tube the arsenic deposits behind the heated part as a metallic coating (*arsenic mirror*). On holding a cold object, *e. g.*, a piece of porcelain, in the flame of the gas, the arsenic forms a black deposit (arsenic spots). In its chemical behavior arsine is very similar to phosphine; its basic properties are very slight, and it does not furnish any derivatives with the halogens.

According to analysis, arsine consists of 1.01 parts by weight of hydrogen and 25 parts of arsenic. If, because of its analogy to phosphine, we ascribe it the formula AsH_3, then the atomic weight of arsenic would be 75 ($= 3 \times 25$) and the molecular weight of AsH_3 would equal 78.03. A determination of the density confirms this. The formula, too, shows that 3 volumes of hydrogen are present in 2 volumes of AsH_3:

$$\underset{\text{2 vols.}}{2AsH_3} \quad \text{contain} \quad \underset{\text{3 vols.}}{3H_2}.$$

We can satisfy ourselves of this by decomposing the gas by electricity in a eudiometer (see p. 120).

Marsh's Method for the Detection of Arsenic.—The method described for the preparation of arsine and the ease with which it is recognized make it possible to detect arsenic in its compounds with great certainty. This is a very important task because of the ready accessibility and frequent use of poisonous arsenic derivatives. Hydrogen is generated in a flask (Fig. 56, a) by the interaction of dilute sulphuric acid and zinc, when the material presumed to contain arsenic is introduced through the funnel tube b. The gas evolved, a mixture of hydrogen and arsine, is then conducted through a calcium chloride drying tube (c) and escapes through the tube of hard glass contracted at several points (d). Upon igniting the escaping hydrogen (after all the air has been previously expelled from the vessel, as otherwise oxyhydrogen gas will be present) it will burn with a bluish-white flame, if arsenic be present, and at the same time disseminate a white vapor. The dark arsenic spots are obtained by holding a cold porcelain dish in the flame. If the tube d be heated (as shown in Fig. 56), an arsenic mirror will be formed upon the adjacent contraction. The slightest traces of arsenic may be detected by this method.

Besides the ordinary arsine, AsH_3, we might expect the existence of As_2H_4 and As_4H_2, corresponding to the liquid and solid phosphines (P_2H_4 and P_4H_2). The first is not known; its derivatives exist, and contain hydrocarbon groups instead of hydrogen. An example of this class is cacodyl, $As_2(CH_3)_4 = (CH_3)_2As{-}As(CH_3)_2$. Nitrogen affords similar compounds—$(CH_3)_2N{-}NH_2$ and $(CH_3)NH{-}NH_2$, derived from diamide or hydrazine, $N_2H_4 = H_2N{-}NH_2$ (p. 131).

The **solid arsine,** As_4H_2, is obtained by the action of nascent hydrogen upon arsenic compounds in the presence of nitric acid. It forms a reddish-brown powder, which decomposes when heated. Retgers considers that the brown color of the arsenic spots and mirror is due to solid arsine, soluble in caustic potash.

COMPOUNDS OF ARSENIC WITH THE HALOGENS.

These are perfectly analogous to the corresponding phosphorus compounds, and are the result of the direct union of their constituents. The fluoride, in union with potassium fluoride, is the only known representative of the compounds corresponding to the formula AsX_5 (see p. 141). The metallic character of arsenic is shown by the fact that arsenic chloride, like other metallic chlorides, may be obtained by the action of hydrochloric acid upon the oxide:

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O.$$

Arsenic chloride is evolved when a solution of the trioxide is boiled with concentrated hydrochloric acid.

Arsenic Trichloride, $AsCl_3$, is a colorless, oily liquid, fuming in the air, and having a specific gravity of 2.2. It solidifies at lower temperatures, melts at —18° and boils at 130°. Its vapor density corresponds to the molecular formula $AsCl_3 = 181.35$. It dissolves in a small quantity of water without change, while much water converts it into the oxide and hydrochloric acid

$$2AsCl_3 + 3H_2O = As_2O_3 + 6HCl.$$

Arsenic Tribromide, $AsBr_3$, is a white crystalline mass, melting at 20°, and boiling at 220°. The **Tri-iodide**, AsI_3, forms red crystals, which melt at 146°. The **Trifluoride**, $AsFl_3$, is a liquid, fuming strongly in the air; it boils at 63°. It results in the distillation of the trichloride or trioxide with calcium fluoride and sulphuric acid.

4. ANTIMONY.

Atom: $Sb = 120$.

The metallic character exhibited by arsenic becomes more distinct with antimony, which at the same time retains its complete analogy to the metalloidal elements, arsenic and phosphorus. Antimony is a perfect metal so far as its physical properties are concerned.

It (stibium) occurs in nature chiefly in union with sulphur, as stibnite, Sb_2S_3 (Japan, Hungary), and with sulphur and metals in many ores. It is almost always accompanied by arsenic. To prepare antimony, stibnite is roasted in a furnace, *i. e.*, heated with air access, whereby the sulphur burns, and antimony trioxide remains:

$$2Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2.$$

The residual oxide is ignited with carbon, which reduces it to metal (general procedure for the separation of metals). Antimony may also be obtained by heating its sulphide with iron, which combines with the sulphur:

$$Sb_2S_3 + 3Fe = 2Sb + 3FeS.$$

The resulting commercial crude antimony is further purified in the laboratory by fusing it with niter, whereby the admixed arsenic, sulphur, and lead are removed. Chemically pure antimony is obtained by reducing the pure oxide.

It is a silver-white and very brilliant metal, of leafy crystalline structure; specific gravity 6.71. Like arsenic it crystallizes in rhombohedra, is very brittle, and may be easily broken. It fuses at 430°, and vaporizes between 1500 to 1700°. The density of its vapor shows that the antimony molecule, unlike that of phosphorus, consists not of four atoms, but rather, like arsenic at the same temperature, of two atoms [Biltz, Z. f. phys. Chem. **19** (1896), 385]. It is not altered in the air at ordinary temperatures, but when heated it burns with a blue flame, yielding white vapors of antimony oxide, Sb_2O_3. Like phosphorus and arsenic it combines directly with the halogens; powdered antimony inflames in chlorine gas. It is insoluble in hydrochloric acid; nitric acid oxidizes it (depending upon its strength and the temperature) to antimony oxide or antimonic acid.

Hydrogen Antimonide—*Stibine*—SbH_3, is produced like arsine, and is very similar to the latter. It has thus far only been obtained mixed with hydrogen. It is a colorless gas of peculiar odor, and when ignited burns with a greenish-white flame, disseminating white vapors of antimony oxide, Sb_2O_3. A red heat decomposes it into antimony and hydrogen. In Marsh's apparatus (Fig. 56, p. 144) it forms an antimony mirror and spots. The mirror is distinguished from that of arsenic by its black color, lack of luster, its insolubility in a solution of sodium hypochlorite (NaClO), and by its slight volatility in a current of hydrogen.

Arsine is also liberated from alkaline solutions in which hydrogen is being generated, *e. g.*, caustic potash and zinc. This is not the case with stibine.

COMPOUNDS OF ANTIMONY WITH THE HALOGENS.

Antimonous Chloride—*Antimony Trichloride*—$SbCl_3$, results from the action of chlorine upon the metal or its sulphide (Sb_2S_3); better by the solution of the oxide or sulphide in strong hydrochloric acid:

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

This solution is evaporated to dryness and the residue distilled.

It is a colorless, crystalline, soft mass (*Butyrum antimonii*), melting at 73° and boiling at 223°. Its vapor density corresponds to the molecular formula, $SbCl_3 = 226.35$. In the air it attracts water and deliquesces. It dissolves unchanged in water acidified with hydrochloric acid. Much water decomposes it; the solution becomes turbid and a white powder—powder of Algaroth (so named in honor of an Italian physician, Victor Algarotus, who used it as a medicine)—separates:

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

The composition of this powder varies with the conditions under which it is formed, but generally corresponds to the formula $2(SbOCl) . Sb_2O_3$. Pure **Antimony Oxychloride**, SbOCl, obtained by heating antimony trichloride with alcohol, occurs in colorless crystals and is further decomposed by water into basic oxychlorides.

While the metallic chlorides are not decomposed by water at ordinary temperatures, the ready decomposition of the halogen derivatives of antimony shows that this element still possesses a partial metalloidal character.

Antimonic Chloride—*Antimony Pentachloride*—$SbCl_5$, results from the action of an excess of chlorine upon antimony or the trichloride. It is a yellowish liquid which fumes in the air, becomes crystalline when cold and melts at —6°. Heat partly decomposes it, like phosphorus pentachloride, into antimonous chloride and chlorine:

$$\underset{\text{1 vol.}}{SbCl_5} = \underset{\text{1 vol.}}{SbCl_3} + \underset{\text{1 vol.}}{Cl_2}.$$

It may be gasified without decomposition at 218° and 58 mm. pressure. Its density corresponds to the formula $SbCl_5$.

Water converts it into pyroantimonic acid ($H_4Sb_2O_7$), and hydrochloric acid. It combines with one molecule of water, forming the crystallizable hydrate $SbCl_5 . H_2O$, melting at about 90°, and with four molecules to a hard, crystalline mass, $SbCl_5 . 4H_2O$ [Anschütz and Evans, Ann. Chem. 239 (1887), 285]. The metallic nature of antimony shows itself in the formation of these hydrates. Neither of the two chlorides of non-metallic phosphorus forms a hydrate; both are immediately decomposed by a little water with the production of hydrochloric acid.

Antimony Tribromide, $SbBr_3$, is a white, crystalline substance, melting at 93° and distilling at 275°. The **Tri-iodide**, SbI_3, is a red compound, *crystallizing* in three distinct forms. It melts at 166° and boils at 400°. The **Pentiodide**, SbI_5, is dark brown in color and melts at about 78°.

Antimony Trifluoride, $SbFl_3$, obtained by the solution of antimony oxide in hydrofluoric acid, crystallizes in colorless rhombic pyramids. It deliquesces on exposure to the air. It is not decomposed by cold water. Its compound with ammonium sulphate is used as a mordant in dyeing.

Antimony Pentafluoride, $SbFl_5$, is a gummy mass. It forms well-crystallizing double salts with the salts of organic bases.

We must also include **Bismuth**, Bi = 208.5, in the group of nitrogen, phosphorus, arsenic, and antimony. Its halogen derivatives resemble those of arsenic and antimony in many respects, *e. g.*, $BiCl_3$, BiI_3, $BiOCl$. Its metallic character, however, considerably exceeds its metalloidal. Thus, it does not unite with hydrogen, and bismuth oxide (Bi_2O_3), similar in constitution to the acid-forming arsenious oxide, As_2O_3, possesses only basic properties. We will, therefore, consider bismuth and its derivatives with the metals.

TABULATION OF THE ELEMENTS OF THE NITROGEN GROUP.

The elements belonging here—nitrogen, phosphorus, arsenic, antimony—present similar graded differences in their physical and chemical properties, just like the elements of the chlorine and oxygen groups, and this gradation is intimately connected with the atomic weights. As the latter increase the substance condenses, the fusibility and volatility decrease, and the similarity to the real metals becomes more prominent.

	N	P	As	Sb
Atomic weight, ...	14.04	31.0	75	120
Specific gravity, ...	0.9 (solid)	1.8–2.1	4.7–5.7	66.7
Melting point, ...	—214° (60 mm.)	44°	red-white heat	
Vapor density ($O_2 = 32$), . .	28.08	124.0	150	240

These elements do not resemble one another in chemical properties as the halogens resemble one another, or as sulphur, selenium and tellurium. Arsenic and antimony alone show chemical kinship. What is exceedingly striking is the difference between the remarkable activity of phosphorus in its yellow variety and the sluggish nitrogen with which red phosphorus may be compared. This difference manifests itself in many of their derivatives as has been observed with their halides (NCl_3, NI_3—PCl_3, PI_3), and will again be seen in their oxygen compounds.

Excepting bismuth, which is perfectly metallic in its nature, the elements of this group form gaseous compounds with three atoms of hydrogen. Ammonia (NH_3) possesses strongly basic properties, and combines with all acids to yield ammonium salts; phosphine (PH_3) combines at the ordinary temperature only with hydrogen bromide and hydrogen iodide to form salt-like compounds. Arsine and stibine no longer show basic properties. Arsenic and antimony, as well as the two preceding elements, combine with the hydrocarbons (*e. g.*, CH_3 and C_2H_5) and form compounds which are analogous in constitution and similar in character to the hydrides. These compounds [$As(CH_3)_3$ and $Sb(CH_3)_3$] will be described in Organic Chemistry; they possess basic properties and yield salts corresponding to the ammonium salts. Compounds of arsenic and antimony corresponding to hydroxylamine and hydrazoic acid are not known.

The oxygen derivatives of these elements exhibit a gradation similar to that of the hydrogen compounds. With increase of atomic weight, corresponding to the addition of metallic character, the oxides which form strong acids in the lower series acquire a more basic nature in the higher series.

CARBON GROUP.

The two non-metals, carbon and silicon, and the metals, tin and germanium, comprise this group. They unite with four atoms of hydrogen or with four atoms of the halogens.

1. CARBON.

Atom: C = 12.00.

Carbon occurs free in nature as the diamond and graphite. It constitutes the most important ingredient of all the so-called organic substances originating from the animal and vegetable kingdoms, and is especially contained in the fossilized products arising from the slow decomposition of vegetable matter—in peat, in lignite, in bituminous coal, and in anthracite. In combination with hydrogen it forms the so-called mineral oils—petroleum and asphaltum. It occurs, further, as carbon dioxide (CO_2) in the air and in many waters; and in the form of carbonates (marble, calcite, dolomite) comprises many minerals and entire rock formations.

It is found in different allotropic modifications when free; these may be referred to the three principal varieties—diamond, graphite and amorphous carbon. In all these forms it is a solid, even at the highest temperatures; non-fusible and only volatile at about 3500° in the electric arc. This deportment can only be explained by the supposition that its molecules are composed of a large number of carbon atoms (see p. 106). All the modifications of carbon are quite stable, but not very reactive. When burned all yield carbon dioxide.

1. The *diamond* occurs in alluvial soils in certain districts (in India, Brazil, and South Africa); less frequently in itacolumite, micaceous schist, and xanthophyllite. It was observed recently in meteoric iron from Cañon Diablo. It has great luster, strong power of refraction, and the greatest hardness of all substances. It crystallizes in forms of the regular system, which are mostly rhombic dodecahedra, rarely octahedra. Ordinarily, it is perfectly colorless and transparent; sometimes, however, it is colored by impurities. Its specific gravity equals 3.5. It does not soften unless exposed to the most intense heat—between the poles of a powerful galvanic battery. It is then converted into a graphitic mass. When heated in oxygen gas to 700–800° it burns to carbon dioxide [see Ber. 23 (1890), 2409]. It is scarcely attacked at all when acted upon by a mixture of nitric acid and potassium chlorate.

The diamond has been made artificially. Molten iron dissolves carbon, which separates on cooling, mostly in the form of graphite. If iron, at high temperature, be saturated with carbon and then be quickly cooled so that its inner portions are subjected to great pressure because of the contraction of the exterior, upon sudden chilling, the carbon then crystallizes in the form of the diamond (Moissan). Molten olivine (magnesium silicate) also dissolves carbon, which again separates on cooling in the form of little diamond crystals.

2. *Graphite* (*γράφειν*, to write) is characterized by its oxidation to graphitic acid when it is heated with a mixture of potassium chlorate and nitric acid. Like amorphous carbon, it is oxidized to mellitic acid by an alkaline solution of potassium permanganate, or when it is made the positive electrode in the electrolysis of alkaline solutions. (See Richter's Organic Chemistry.) Native graphite is found in the oldest rock formations, and of especially good quality at Altai, in Siberia. It occurs, too, in considerable quantities at many places in the United States. It is occasionally found crystallized in six-sided forms, but usually as an amorphous, grayish-black, glistening, soft mass, used in the manufacture of lead pencils. The specific gravity is 2.25. It conducts heat and electricity well. When away from air contact it is not altered even at the highest temperatures. It is the only variety of carbon stable at high temperatures; when heated the other varieties pass into it. It usually burns when heated in an atmosphere of oxygen, but with more difficulty than the diamond, forming carbon dioxide, and leaving about 2–5 per cent. of ash. To purify the poorer and more impure kinds of graphite, they are pulverized and heated with a mixture of potassium chlorate and sulphuric acid; the product is washed with water, and the residue ignited (Brody's graphite).

Luzi claims two varieties of graphite: *graphitite* and the *true graphite.* The first does not swell up when moistened with red, fuming nitric acid, and is then strongly ignited (Passauer and Siberian graphite). The true graphites do swell up under similar treatment (graphite from Ceylon, New York, Ticonderoga); see Ber. 26 (1893), 890.

Graphite may be obtained artificially by fusing amorphous carbon with iron; when the latter cools, a portion of the dissolved carbon separates in hexagonal shining leaflets.

3. *Amorphous carbon* (α, privative, and μορφή, form), is produced by the carbonization of organic (containing carbon) substances, and is found in a fossilized state. Nitric acid and potassium chlorate convert it in the cold into brown substances soluble in water. The purest amorphous carbon is soot, which is obtained by the imperfect combustion of resins and oils (like turpentine) rich in carbon. *Gas carbon*, called metallic carbon, deposits in the manufacture of gas in the retorts, and is very hard, possessing metallic luster, and conducting electricity well; hence its use in galvanic batteries. *Coke*, resulting from the ignition of bituminous coal, forms a sintered mass, conducting heat and electricity well. *Charcoal* is very porous, and can absorb many gases and vapors; 1 volume of it condenses 90 volumes of ammonia, 55 volumes of hydrogen sulphide, and 9 volumes of oxygen. At 100°, and under the air-pump, the absorbed gases are again liberated. Charcoal will also take up many odorous substances and decaying matter; hence it is employed as a disinfectant. *Animal charcoal* is obtained by the carbonization of animal matter (bones, blood, etc.), and possesses the power of removing many coloring substances from their solutions; hence it serves in the laboratory and in commerce for the decolorization of dark solutions.

All these varieties of carbon contain smaller or larger quantities of nitrogen, hydrogen, and mineral substances, which remain as ash after combustion. Hydrochloric acid will withdraw almost all the mineral constituents.

The fossil coal varieties, bituminous coal, lignite and turf, are the products of a peculiar, slow decay of wood fiber, which gradually separates oxygen and hydrogen, and enriches itself in carbon. Fossil coal contains 90 per cent. and lignite 70 per cent. of carbon. The fossil coal richest in carbon, the last product of the alteration, is *anthracite*. This has lost all its organic structure, and contains 96–98 per cent. of carbon.

COMPOUNDS OF CARBON WITH HYDROGEN.

With hydrogen, carbon forms an unlimited number of compounds, into which all other elements, especially oxygen and nitrogen, can enter. The derivatives of carbon have been termed *organic compounds*, because they were formerly obtained exclusively from vegetable and animal organisms, and the idea was entertained that they were produced by the influence of forces other than those forming the mineral substances. At present, most carbon derivatives are prepared artificially from the elements by simple synthetic methods; we are aware that they do not differ essentially from mineral substances. Hence the description of the carbon compounds must be arranged in the general system of chemical bodies. This, however, is not readily executed without sacrificing the review of a defunct system. The derivatives of carbon are so numerous, and possess so many peculiarities, that it appears necessary, from a practical standpoint, to treat them apart from the other compounds, in a separate portion of chemistry, which we, pursuing the old custom, term organic chemistry. We then designate the chemistry of *all other bodies* as *Inorganic Chemistry*. Only the simplest carbon compounds will be considered here.

It is only under the influence of the electric arc that the direct union of carbon and hydrogen can be effected; the product is acetylene (C_2H_2). All other hydrocarbons are obtained indirectly in various ways.

Methane—*Marsh Gas*—CH_4. This simplest hydrocarbon is that chemical compound which is richest in hydrogen; it contains 25.18 per cent. It is formed in the decay of organic matter under water (in swamps, hence called marsh gas, and in coal mines), and escapes in large quantities in many regions of the earth (thus at Baku, on the Caspian Sea, in Pennsylvania and in Ohio, where the gases escaping from petroleum wells contain as much as 90–97 per cent. of methane). It is produced in the dry distillation of coal, wood, petroleum and other organic substances; hence is a constituent of illuminating gas. It may be obtained synthetically by conducting vapors of carbon bisulphide and hydrogen sulphide over ignited copper filings:

$$CS_2 + 2H_2S + 8Cu = 4Cu_2S + CH_4.$$

For its preparation, heat a mixture of sodium acetate with sodium hydroxide:

$$C_2H_3O_2Na + NaOH = CH_4 + Na_2CO_3.$$

Its formation from aluminium carbide by the action of water is rather interesting. Aluminium hydroxide is also produced (Moissan):

$$Al_4C_3 + 6H_2O = 2Al_2O_3 + 3CH_4.$$

Methane is a colorless, odorless gas, insoluble in water. Its density corresponds to the molecular formula CH_4. Methane, under great pressure and at low temperatures (below —82°, p. 48), is condensed to a colorless liquid, which boils at —164° under the ordinary pressure. Its specific gravity is 0.415 at the boiling point. When ignited it burns with a faintly luminous flame. It affords a violently explosive mixture (fire-damp of the miners) with two volumes of oxygen (or ten volumes of air):

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{2 vols.}}{2H_2O}.$$

MOLECULAR FORMULA OF METHANE. ATOMIC WEIGHT OF CARBON.

The quantitative analysis of methane shows that for every 1.01 parts of hydrogen in it there are 3 parts of carbon. Were the formula CH (analogous to hydrochloric acid) then the atomic weight of carbon would be 3. If it corresponded to the formula of water (H_2O) or ammonia (NH_3) then the atomic weight of carbon would equal 6, or 9:

$H = 1.01$	$2H = 2.02$	$3H = 3.03$	$4H = 4.04$
$C = 3$	$C = 6$	$C = 9$	$C = 12$
$CH = 4.01$	$CH_2 = 8.02$	$CH_3 = 12.03$	$CH_4 = 16.04$

All these and many other formulas agree with the analytical results. The gas density, however, decides in favor of the formula CH_4, because a liter of methane weighs under normal conditions 0.71464 gram and this would make the molecular weight, referred to $O_2 = 32$ (see p. 79), $\frac{0.71464}{0.04466} = 16.0$.

That the atomic weight of carbon is really 12, is proven by the fact *that of all its innumerable derivatives, not one contains in its molecule less than 12 parts, by weight* (*therefore in the mol-volume* (p. 98) *not less than 12 grams*), *of this element.* It follows, with certainty, from the periodic system of elements.

From the formula CH_4 it follows that in 1 volume of methane there are 2 volumes of hydrogen:

$$\underset{\text{1 vol.}}{CH_4} \text{ contains } \underset{\text{2 vols}}{2H_2}$$

This is proved indirectly by the combustion of methane with oxygen in a eudiometer (see p. 137). Four atoms of hydrogen yield two molecules of water; one atom of carbon yields one molecule of carbon dioxide, CO_2 Hence the volume relation in the combustion of methane in oxygen is expressed by the equation:

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{2 vols.}}{2H_2O}.$$

In 2 volumes of aqueous vapor there are 2 volumes of hydrogen; hence in 1 volume of CH_4, there are 2 volumes of H_2. The result of the eudiometric analysis confirms these conclusions

Ethane or Ethyl Hydride, C_2H_6, is formed when hydrogen *in statu nascendi* acts upon ethyl bromide:

$$C_2H_5Br + H_2 = C_2H_6 + HBr,$$

or by the action of potassium or sodium upon methyl iodide (p. 159):

$$2CH_3I + Na_2 = C_2H_6 + 2NaI.$$

This is a colorless gas, insoluble in water, and when ignited it burns with a feebly luminous flame. Liquid ethane boils at —89.5° under 735 mm. pressure.

Besides methane (CH_4) and ethane (C_2H_6) there exists a long series of hydrocarbons of the general formula C_nH_{2n+2} (*e. g.*, C_3H_8, C_4H_{10}, C_5H_{12}, etc.), in which each member differs from the preceding and next following by 1C and 2H (CH_2). Bodies belonging to such a series, greatly alike in their chemical behavior, are termed *homologues* (*ὁμοῖος*, similar; *λόγος*, nature of the affair). In addition to this series of *saturated* hydrocarbons others exist, with less hydrogen, and by the addition of the latter, pass into the *saturated*, and may, therefore, be termed *unsaturated*. The first *unsaturated* series has the formula C_nH_{2n}, the second, the formula C_nH_{2n-2}, etc. The lowest member of the series C_nH_{2n} is ethylene (see Chemical Structure, p. 168).

Ethylene, C_2H_4, is formed in the destructive distillation of wood, bituminous coal, and many carbon compounds, hence is contained in illuminating gas. It is most easily obtained by the action of sulphuric acid upon alcohol, whereby the acid withdraws the elements of water from the latter:

$$\underset{\text{Alcohol.}}{C_2H_6O} - H_2O = \underset{\text{Ethylene.}}{C_2H_4}.$$

It is a colorless gas, of weak, ethereal odor. Its critical temperature is +10°, and its critical pressure, 51 atmospheres. Under a pressure of 1 atmosphere, liquid ethylene boils at —102°, and when in a vacuum at —150°. It solidifies at —160°. As it does not solidify on vaporizing, it is well adapted for the liquefaction of other gases (p. 48). It burns with a bright, luminous flame, decomposing first into marsh gas and free carbon:

$$C_2H_4 = CH_4 + C.$$

The methane then burns and heats the particles of carbon in the flame to incandescence; these are then consumed to carbon dioxide (CO_2) (see Ber. 26 (1893), III, 9).

The unsaturated compound, ethylene, unites directly with two atoms of chlorine and of bromine:

$$C_2H_4 + Cl_2 = C_2H_4Cl_2.$$

The resulting compounds, $C_2H_4Cl_2$ and $C_2H_4Br_2$, are oily liquids; hence the name *olefiant gas* for ethylene.

The first member of the second unsaturated series is acetylene, C_2H_2.

Acetylene is produced in the dry distillation of many carbon compounds, and is present in coal gas, to which it imparts a peculiar penetrating odor. It is also formed in the incomplete combustion of coal gas—*e. g.*, when the flame of a Bunsen burner strikes back. Berthelot synthesized acetylene by causing the electric spark to strike across from carbon points in an atmosphere of hydrogen:

$$C_2 + H_2 = C_2H_2.$$

No other hydrocarbon has as yet been directly built up from its elements.

The production of acetylene by the action of water or dilute acids upon metallic carbides is very interesting, *e. g.*, from calcium carbide:

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

Pure acetylene is a colorless gas with a peculiar odor. It can be readily condensed. Its critical temperature is 37°; its critical pressure equals 68 atmospheres. At 0° it may be liquefied by a pressure of 21.5 atmospheres. Liquid acetylene boils at —83°. When it is poured it changes in part to a snow-like, combustible mass. At 19.5°, 1 kilogram of liquid acetylene will yield 896 liters of gas under the ordinary atmospheric pressure. At medium temperatures it dissolves in an equal volume of water; therefore, it must be collected over strong salt solutions. It is very soluble in acetone, 1 volume of the latter dissolving 25 volumes of acetylene at the ordinary temperature and pressure.

Being an unsaturated hydrocarbon it combines with chlorine; with two or four atoms of the same:

$$C_2H_2Cl_2, C_2H_2Cl_4.$$

It is chemically very much like hydrazoic acid (p. 132). It possesses acid properties but these are not so pronounced as in the case of hydrazoic acid; acetylene and many of its metallic derivatives are explosive (p. 31).

As a result of observations made by Willson, an American, when attempting to prepare the alkaline earth metals by the reduction of their oxides with carbon in the electric furnace, calcium carbide has been made since 1894 on a large scale, for the purpose of producing acetylene by the method employed by Moissan. As acetylene is now so readily accessible it plays an important rôle as an illuminant. It burns, on issuing from a small aperture under a definite pressure, with a blinding white flame, almost free from soot. As it is readily condensed it is especially adapted for the illumination of vessels, trains, etc.

Mixtures of acetylene with from 1.25 to 20 volumes of air are explosive; a most powerful explosion will occur when the proportion is 1 volume of acetylene and 12 volumes of air. The acetylene prepared from commercial calcium carbide usually contains hydrogen sulphide and phosphide.

Compare: Fr. Liebetanz, Calciumkarbid und Acetylentechnik, 2. Aufl., Leipzig, 1899; F. Dommer, Calciumkarbid und Acetylen; deutsch von Landgraf, München und Leipzig, 1898.

The three hydrocarbons considered above, methane (CH_4), ethylene (C_2H_4), and in slight amount acetylene (C_2H_2), constitute, together with hydrogen and carbon monoxide (CO), ordinary *illuminating gas*, which is produced in the dry distillation of bituminous coal, lignite, or wood. The illuminating power is influenced by its quantity of ethylene and acetylene (and their homologues).

Late investigations indicate that all hydrocarbons are broken down by the heat of the flame into acetylene and carbon, which then burn and become luminous (see Z. f. anorg. Ch. 9 (1895), 233).

THE NATURE OF FLAME.

We are aware that every chemical union which occurs in a gaseous medium, and is accompanied by the evolution of light is designated combustion. Some bodies, like sulphur and phosphorus, yield a flame when burned in the air or in other gas; such substances are converted into gases or vapors at the temperature of combustion. Pure carbon burns without a flame, becomes incandescent, because it is non-volatile. The carbon compounds, wood, bituminous coal, and tallow, are, indeed, not volatile, but burn with a flame because under the influence of heat they develop combustible gases. Flame is, therefore, nothing more than a combustible gas heated to incandescence. We know, too, that hydrogen burns in oxygen and chlorine, conversely, oxygen and chlorine will burn in hydrogen (p. 57), and that illuminating gas burns in the air, therefore air (its oxygen) burns in the former. This may be demonstrated in the same manner as in the case of chlorine and hydrogen.

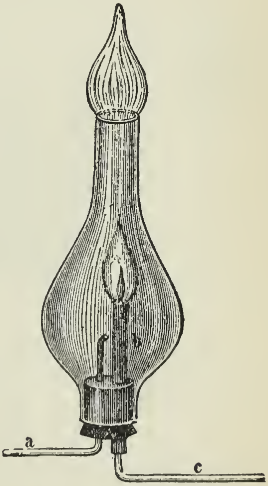


FIG. 57.

The relative combustibility and the so-called return of the flame may be very plainly illustrated by means of the following contrivance: An ordinary lamp chimney (Fig. 57) is closed at its lower end with a cork, through which two tubes enter; the narrow tube, *a*, somewhat contracted at its end, is connected with a gas stop-cock; the other tube, *b* (best a cork-borer), is about 5 mm. wide, and communicates with the air. The gas issuing from the tube *a* is ignited, and the chimney is then dropped over the not too large flame; it continues to burn along quietly, as sufficient air enters through the wide tube *b*. Upon increasing the supply of gas, the flame becomes larger, the globe fills with illuminating gas, while the air is displaced. The gas flame is extinguished, and an air flame appears upon the wider tube, *b*, as the entering air continues to burn, in the atmosphere of illuminating gas. The excess of the latter escaping from the upper portion of the globe may be ignited, and we then have a gas flame above, while within the globe we have an air flame. On again lessening the gas flow the air flame will distribute itself, extend to the exit of the tube *a*, and then the gas flame will appear upon the latter, while the flame above the globe is extinguished. In this manner, we may repeat the return process of flames at will. That the air actually burns in the air flame may be plainly proved if we introduce a small gas flame from *c*, through the wide metallic tube *b*; the little flame will continue to burn in the air flame, but will be extinguished if it be introduced higher up into the atmosphere of illuminating gas.

We say ordinarily that only those bodies are combustible which burn in an atmosphere of oxygen or in air. If we imagine, however, an atmosphere of hydrogen, or illuminating gas, then bodies rich in oxygen must be combustible in these. In fact, nitrates, chlorates, etc., burn in an atmosphere of illuminating gas with the production of an oxygen flame. This may be demonstrated as follows: An Argand lamp chimney (Fig. 58) is closed at its lower end with a cork, bearing a gas-conducting tube. The gas which escapes through the opening of the metal cover, a, is ignited. Then the substance (potassium or barium chlorate, etc.) is introduced into the flame on an iron spoon provided with a long handle, heated to the temperature of decomposition (disengagement of oxygen), and the spoon then plunged through the opening into the gas atmosphere. The substance burns with a brilliant light, and gives a characteristic flame reaction.

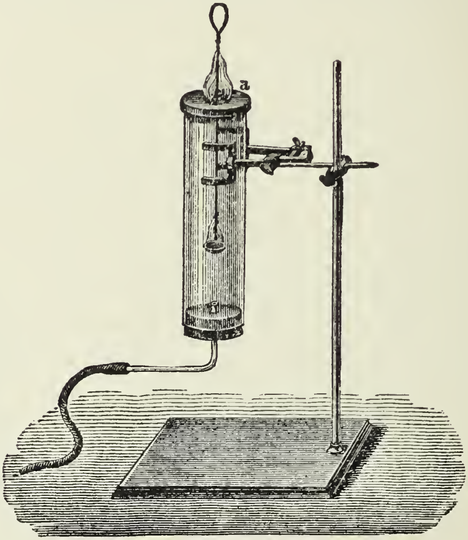


FIG. 58.

The brilliancy or *luminosity* of a flame is influenced by the nature of the substances contained in it, also by their temperature and density. Incandescent gases shine very faintly *per se;* this is especially true when they are diluted. Thus hydrogen, ammonia and methane burn with a pale flame. Even sulphur burns in the air with a slightly luminous flame. If, on the contrary, sulphur or phosphine be permitted to burn in pure oxygen, or arsenic and antimony in chlorine gas, an intense display of light follows. This depends on the fact that the flame is not diluted by the nitrogen of the air, and therefore develops a higher temperature. That the density of the gas of flames exercises a great influence upon the luminosity is proved by the fact that hydrogen, compressed into a smaller space with oxygen, burns with intense light.

A slightly luminous flame may be rendered intense by introducing solid particles into it. For example, if hydrogen be passed through liquid chromium oxychloride (CrO_2Cl_2) it burns with a bright, luminous flame, because the chromium oxychloride is changed by the high temperature, with the absorption of hydrogen, into water, hydrochloric acid, and solid, non-volatile chromium oxide, whose particles are heated to incandescence by the hydrogen flame. The illuminating power of the various hydrocarbons and carbon compounds is similarly explained. Marsh gas, CH_4, and ethane, C_2H_6, give a pale flame, because they burn directly to aqueous vapor and carbon dioxide; ethylene, on the contrary, burns with a bright, luminous flame, because, by the temperature of combustion, it decomposes first into methane and carbon, whose particles glow in the flame (see p. 153).

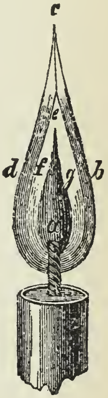


FIG. 59.

Let us consider the flame of an ordinary stearin candle: On approaching the wick with a flame the stearin melts, is drawn up by the fibers and converted into gaseous hydrocarbons, which ignite, and by their chemical union with the oxygen of the air produce the flame. Three zones are distinguishable in this flame. The unaltered gases exist in the inner non-volatile zone *a* (Fig. 59); they cannot burn because of lack of air. If the lower end of a thin glass tube be inserted here the gases will rise in it, and may be ignited at the upper end. There is a partial combustion of the gases in the middle, luminous part, *f*, *e*, *g*; ethylene, C_2H_4, breaks down here into methane, CH_4, and carbon, C; the first burns completely, while the carbon is heated to a white heat, because there is not sufficient oxygen present for its combustion. The presence of carbon particles in the luminous part may be easily proved by placing a cold glass rod or a wire in it; it will at once be covered with soot.

In the outer, very feebly luminous and almost invisible mantle, *b*, *c*, *d*, of the flame, which is completely surrounded by air, occurs the perfect combustion of all the carbon to carbon dioxide.

A perfectly identical structure is possessed by the ordinary illuminating gas flame. By bringing as much air or oxygen into it as is necessary for the complete combustion of all the carbon, none of the latter separates (see p. 158), and there is produced a faintly luminous but very hot flame.

Upon this principle is based the construction of the Bunsen burner, the flame of which is employed in laboratories for heating and ignition. Fig. 60 represents a form of the same. The upper tube, *c*, is screwed into the lower portion, and in the figure is separated merely for the sake of explanation. The gas enters through the narrow opening, *a*, from the side gas tube, and mixes with air in the tube *c*, which enters through the openings of the ring, *b*. In this way we obtain a flame which is but faintly luminous, although affording an intense heat. On closing the openings in *b* the air is cut off, and the gas burns at the upper end of the tube *c* with a bright, strongly smoking flame. The non-luminous flame contains an excess of oxygen, and hence oxidizes—*oxidizing flame*. It is employed to effect oxidation reactions. Its temperature is about 1200°. The luminous flame, on the other hand, is reducing in its action (temperature 1000° C.), and is designated the *reducing flame*, because the glowing carbon in it abstracts oxygen from many substances.

The non-luminosity of the Bunsen burner flame, due to addition of air, depends on a more complete combustion of the separated carbon or of the yet undecomposed hydrocarbons.

Another variety of non-luminosity of hydrocarbon flames is induced by the admixture of inactive gases, like nitrogen and carbon dioxide. By this means the flame is enlarged and the combustion, as in the luminous flame, takes place only in the outer cone; further, the temperature is lowered, and probably does not acquire the decomposition temperature of methane and ethylene. The simple extension of an illuminating flame upon a plate, will render it non-luminous, because then the air comes in contact with a larger flame surface. On heating a gas made non-luminous by the admixture of nitrogen, and then letting it burn, its flame becomes luminous because the increased temperature can induce the decomposition of methane.

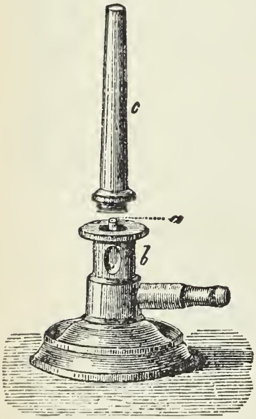


FIG. 60.

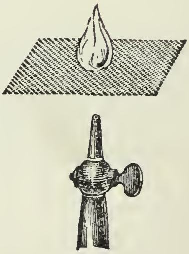


FIG. 61.

In rendering flame non-luminous by carbon dioxide, we must also consider that the same is converted, by the particles of carbon, into carbon monoxide:

$$CO_2 + C = 2CO.$$

Indeed, but a few per cent. of carbon dioxide in a gas flame suffices to considerably diminish its luminosity:

$$\begin{array}{ccccccc} C_2H_4 & + & CO_2 & = & CH_4 & + & 2CO, \\ \text{1 vol.} & & \text{1 vol.} & & \text{1 vol.} & & \text{2 vols.} \end{array}$$

while the presence of nitrogen is far less detrimental.

Every substance requires a definite temperature for its ignition—*temperature of ignition*. When a substance is once ignited it generally burns further, because additional particles are raised to the temperature of ignition by the heat of combustion. By rapid cooling (*e. g.*, by the introduction of a piece of metal into a small flame) every flame may be extinguished. By holding a wire gauze over the opening of a gas lamp, from which gas issues, and igniting the same above the wire (Fig. 61), the latter, being a good conductor of heat, cools the flame so much that it is incapable of igniting the gas below the gauze. Upon this phenomenon depends the construction of Davy's safety lamp, which is used in coal mines to avoid ignition of the fire-damp. It is an ordinary oil lamp surrounded and shut off from the air by a metallic wire gauze. On bringing a lighted lamp of this sort into an explosive mixture, or into a combustible gas (*e. g.*, into a large jar, in which ether is present), the gas penetrating into the lamp will burn, but the combustion will not extend to the external gases.

COMPOUNDS OF CARBON WITH THE HALOGENS.

Carbon combines directly with fluorine alone of the halogens, forming gaseous carbon tetrafluoride, CFl_4. Compounds with all the halogens result, however, by the action of the latter upon the hydrocarbons. We have seen that chlorine and bromine act upon water, ammonia, hydrogen sulphide, etc., in such manner as to unite with the hydrogen to form hydrogen chloride, etc., while the other element is either set free or is also combined with the chlorine (p. 128). Chlorine acts similarly upon the hydrocarbons; here hydrogen is displaced, atom after atom, by chlorine, forming hydrogen chloride and chlorine derivatives:

$$CH_4 + Cl_2 = CH_3Cl + HCl,$$
$$CH_4 + 2Cl_2 = CH_2Cl_2 + 2HCl,$$
$$CH_4 + 3Cl_2 = CHCl_3 + 3HCl, \text{ etc.}$$

Such a process is termed *substitution*, and the products *substitution products*. These halogen derivatives are distinguished from the halides of other non-metals by their comparatively greater stability toward water (see pp. 148, 161). In this way we obtain from methane, CH_4, the products, CH_3Cl, CH_2Cl_2, $CHCl_3$ (chloroform) and finally CCl_4, carbon tetrachloride, a colorless, ethereal liquid, boiling at 76°.

The compound C_2Cl_6, hexachlorethane, obtained by the action of chlorine upon ethane, C_2H_6, is a crystalline mass, melting and boiling at 186°. On conducting its vapors through a red-hot tube they decompose into ethylene tetrachloride and chlorine:

$$C_2Cl_6 = C_2Cl_4 + Cl_2.$$

Ethylene tetrachloride, C_2Cl_4, is a liquid boiling at 122°.

Fluorine, bromine, and iodine yield similar compounds; they will be treated more exhaustively in Organic Chemistry.

The *heats of formation* of the previously mentioned hydrocarbons (from amorphous carbon and hydrogen) are deduced from the heat of combustion, and equal:

$$(C,H_4) = 21.7;\ (C_2,H_6) = 28.6;\ (C_2,H_4) = -2.7;\ (C_2,H_2) -47.8.$$

The absorption of heat in the formation of acetylene, C_2H_2, and ethylene, C_2H_4, is explained by the fact that the solid carbon molecules must first be gasified and separated into atoms in order to unite with hydrogen. The energy requisite for this equals very nearly 39.7 Cal. for 12 parts by weight of amorphous carbon (76.4 Cal. for 24 parts); then the preceding heats of formation must be increased about this amount, in order to express the true heat of formation (from gaseous carbon atoms) of the hydrocarbons.

Beginning with acetylene, C_2H_2, we discover that its conversion into ethylene, C_2H_4, and into ethane, C_2H_6, ensues with heat disengagement:

$$(C_2H_2,H_2) = 45.1;\ (C_2H_4,H_2) = 25.9$$

In accordance with this acetylene readily unites with hydrogen (*in statu nascendi*, or by action of platinum sponge), forming ethylene and ethane.

The *heats of formation* of the carbon chlorides approach those of the hydrogen derivatives very closely:

$$(C,Cl_4\text{-gas}) = 21.0;\ (C_2,Cl_4\text{-gas}) = -1.1$$

2. SILICON.

Atom: Si = 28.4.

Silicon next to oxygen is the most widely distributed element in nature. Owing to its affinity for the latter it does not occur in a free condition. Combined with oxygen as silicon dioxide (SiO_2), and in the form of salts of silicic acid (silicates) it comprises many minerals and almost all the crystalline rocks.

It was first obtained in a free condition by Berzelius (1823) on heating potassium silico-fluoride (K_2SiFl_6) with metallic potassium:

$$K_2SiFl_6 + 4K = 6KFl + Si.$$

The ignited mass is treated with water, which dissolves the potassium fluoride and leaves the silicon as a brown, non-lustrous, *amorphous* powder. It can also be obtained by heating silicon fluoride ($SiFl_4$) with sodium, or very readily by igniting a mixture of quartz sand (silicon dioxide) with magnesium powder [see Cl. Winkler, Ber. **23** (1890), 2652]:

$$2SiO_2 + 2Mg = Si + 2MgO.$$

It burns to silicon dioxide (SiO_2) when heated in the air.

Another modification—the *crystalline silicon*—discovered by St. Claire Deville, is obtained by fusing sodium silico-fluoride with aluminium or with sodium and zinc. The separated silicon dissolves in the molten zinc, and on cooling, deposits out in crystals, which remain on dissolving the zinc in hydrochloric acid. The crystalline product consists of black, shining octahedra and needles, of specific gravity 2.49, and of very great hardness. Upon ignition in the air or oxygen it is not oxidized; it is not attacked by acids. On boiling it with a sodium or potassium hydroxide solution it dissolves, forming a silicate and liberating hydrogen:

$$Si + 4KOH = K_4SiO_4 + 2H_2.$$

Heated in chlorine gas, silicon burns to the chloride.

Hydrogen Silicide, SiH_4, the analogue of CH_4, is produced like arsine and stibine by dissolving an alloy of silicon and magnesium in dilute hydrochloric acid:

$$Mg_2Si + 4HCl = SiH_4 + 2MgCl_2.$$

Such an alloy can be obtained by heating finely pulverized quartz or glass with 1½ times its quantity of magnesium powder. The escaping hydride contains admixed hydrogen, has a disagreeable odor, ignites spontaneously in the air, and burns to the dioxide and water:

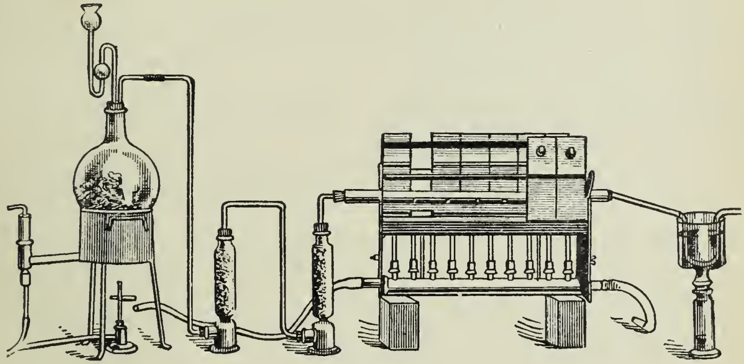


FIG. 62.

$$SiH_4 + 2O_2 = SiO_2 + 2H_2O.$$

Perfectly pure silicide, free from hydrogen, is obtained by heating the compound, $SiH(O.C_2H_5)_3$, which will be described in Organic Chemistry. In the air at ordinary pressure it ignites only upon warming; if, however, the gas, by diminution of pressure or by the addition of hydrogen, is diluted, it becomes spontaneously combustible at the ordinary temperature. A red heat decomposes the hydride into amorphous silicon and hydrogen. When mixed with chlorine it inflames and probably forms substitution products similar to those of methane (CH_4). Pure hydrogen silicide condenses to a liquid at —1° and a pressure of 100 atmospheres.

Silicon Chloride, $SiCl_4$, results from the action of chlorine upon silicon, or magnesium silicide, or by conducting chlorine over an ignited mixture of the dioxide and carbon (Fig. 62):

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

The mixture is placed in a porcelain tube, which is heated to a red heat. The chlorine generated in the flask is dried in the two calcium chloride towers and the silicon tetrachloride is condensed in the receiver chilled with ice-water. While carbon or chlorine does not act separately upon the dioxide, when they act simultaneously the reaction is induced by the mutually supporting affinities of carbon for oxygen and of chlorine for silicon.

Silicon chloride is a colorless liquid, having a specific gravity of 1.5, and boiling at 59°. It fumes in the air, and is decomposed by water into silicic and hydrochloric acids:

$$SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl.$$

This is a remarkable distinction between it and carbon tetrachloride.

Silicon chloride may be employed in determining the atomic weight of silicon. Analysis shows that it contains 7.1 parts of silicon for every 35.45 parts of chlorine. Supposing, from the great analogy of the silicon compounds to those of carbon, that its formula is $SiCl_4$, the atomic weight of the silicon would be 28.4:

$$\begin{array}{rcl} Si & = & 28.4 \\ Cl_4 & = & 141.80 \quad (4 \times 35.45). \\ \hline SiCl_4 & = & 170.20 \end{array}$$

This supposition is confirmed by the vapor density of the chloride and other derivatives of silicon.

Silicon Bromide, $SiBr_4$, and **Silicon Iodide**, SiI_4, are formed in the same manner as the chloride. The first is a colorless liquid, of specific gravity 2.8, becoming solid at —12° and boiling at +153°. The iodide forms colorless octahedra, melting at 120° and boiling at 290°. Like the chloride, both are decomposed by water.

Besides these compounds, which may be viewed as hydrogen silicide, in which all of the hydrogen is replaced by halogens (see p. 159), others exist in which only a part of this element is replaced. Thus, *silicon chloroform*, $SiHCl_3$, corresponds to the chloroform ($CHCl_3$) derived from methane. It is produced by the action of phosphorus pentachloride, or antimony pentachloride, on hydrogen silicide:

$$SiH_4 + 3SbCl_5 = SiHCl_3 + 3SbCl_3 + 3HCl;$$

or upon heating silicon in dry hydrogen chloride gas: in this case a mixture of the tetrachloride and silicon chloroform results (see also Ber. 22, 188). These compounds may be separated by fractional distillation. Silicon chloroform is a colorless liquid, of specific gravity 1.6, and boils at 35–37°. The vapor density corresponds to the molecular formula $SiHCl_3$. It fumes in the air, and decomposes with water into silicic and hydrochloric acids.

The silicon bromoform, $SiHBr_3$, and iodoform, $SiHI_3$, are very similar to chloroform; they correspond to the analogous carbon compounds.

The compounds Si_2Cl_6 and Si_2I_6 are known. They correspond to hexachlorethane, C_2Cl_6. From all these data we observe the analogy, based on formulas alone, between silicon and carbon.

Silicon Fluoride, $SiFl_4$, is formed when hydrofluoric acid acts upon silica:

$$SiO_2 + 4HFl = SiFl_4 + 2H_2O.$$

To prepare it, a mixture of fluorite and powdered glass, or sand (SiO_2), is warmed with sulphuric acid; by the action of sulphuric acid upon the fluorite hydrogen fluoride (p. 64) is disengaged, and this reacts upon the silicon dioxide in the manner indicated in the above equation. The liberated gas is collected over mercury. It is colorless, has a penetrating odor, and fumes strongly in the air. Its vapor density corresponds to the molecular formula $SiFl_4$. Its deportment with water is very characteristic; it is decomposed thereby into silicic acid (H_4SiO_4) and hydrogen silico-fluoride: $3SiFl_4 + 4H_2O = H_4SiO_4 + 2H_2SiFl_6$. For the execution of this method, conduct the tetrafluoride through a glass tube into a vessel containing water (Fig. 63). Gelatinous silicic acid separates out, and the gaseous hydrogen silico-fluoride (H_2SiFl_6) remains dissolved in the water. As the separating silicic acid may easily obstruct the opening of the glass tube, the latter is allowed to project a slight distance into mercury. The solid silicic acid is separated from the aqueous solution by filtration.

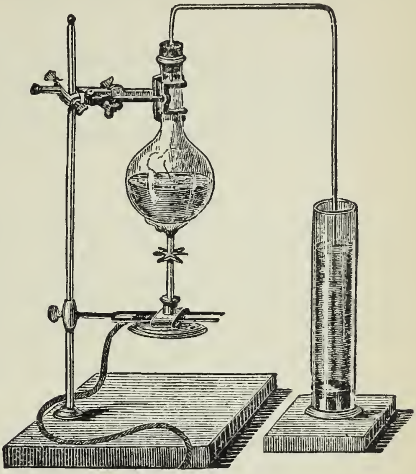


FIG. 63.

Hydrogen Silico-fluoride, H_2SiFl_6, is only known in aqueous solution. Upon evaporation at a low heat it decomposes into the tetrafluoride and hydrofluoric acid ($SiFl_4$ and $2HFl$). In its chemical deportment it is an acid similar to the hydrogen-halogen acids. Its aqueous solution reddens blue litmus-paper, dissolves many metals, and saturates bases, forming salts with them, in which two hydrogen atoms are replaced by metal. The potassium and barium salts dissolve with difficulty in water.

Silicon Carbide, Carborundum, SiC. This remarkable substance was discovered by Acheson when, at the suggestion of Edison, he endeavored to dissolve carbon in fused and highly heated aluminium silicate, hoping that when the mass cooled diamonds would appear. Mühlhäuser determined its composition. Carborundum is produced by heating a mixture of sand and coke, with salt as a flux, in the electric furnace to about 3500°: $SiO_2 + 3C = SiC + 2CO$. When pure it consists of brilliant green crystals of specific gravity 3.22. It is insoluble in the ordinary solvents and burns with difficulty even in oxygen. It is attacked by molten caustic alkalies and alkaline carbonates. In hardness it ranks next to boron carbide and the diamond; hence it is beaten into powder and used as an abrasive, superior to anything known at present in this line. See Metallic Carbides; also Z. f. anorg. Ch. 5 (1894), 104; O. N. Witt, Die chemische Industrie auf der Kolumbischen Weltausstellung zu Chikago (1894), 124; F. Ahrens, Die Metallkarbide und ihre Verwendung, Stuttgart, 1896.

The *heats of formation* of the halogen derivatives of silicon are as follows:

$$(Si,Cl_4) = 157.6;\ (Si,Br_4) = 120.4;\ (Si,I_4) = 58.0.$$

Their ready decomposability by water may be accounted for if the heat of formation of silicic acid be considered: $Si, O_2 = 219.0$ Cal. Their deportment toward oxygen is also very interesting. The heat disengagement, in their transposition, following the equation

$$SiX_4 + O_2 = SiO_2 + 4X,$$

equals 61.4 Cal., with the chloride, 98.6 Cal., with the bromide and with the iodide 161.0 (= 219–58) Cal. Therefore, oxygen must liberate the halogen atoms present in them. And this occurs with the chloride and bromide when raised to a red heat, while the iodide inflames in the air, yielding silicon dioxide and iodine vapor.

TIN, Sn = 118.5, and the recently discovered (1886) GERMANIUM, Ge = 72, attach themselves in chemical character to the group containing carbon and silicon. They bear the same relation to the latter elements which arsenic and antimony bear to the members of the nitrogen group. This is evident in their atomic weights:

N = 14.04	P = 31.0	As = 75	Sb = 120
C = 12.00	Si = 28.4	Ge = 72	Sn = 118.5.

Germanium and tin, like carbon and silicon, form volatile compounds with four atoms of the halogens, *e. g.*, $GeCl_4$ and $SnCl_4$. In a similar manner they unite with oxygen to yield dioxides, *e. g.*, GeO_2 and SnO_2, which resemble silicon dioxide in having an acid character. On the other hand, they do not form volatile hydrogen derivatives, and are thus markedly distinguished from the other non-metals. Therefore germanium and tin, with their higher analogue, LEAD, will be treated with the metals.

In the preceding pages we have considered four groups of elements, comprising all the so-called metalloids (with the exception of boron). In each group the last members, possessing the highest atomic weights, exhibit very distinct metallic properties. This is clearly the case with germanium and tin, antimony and arsenic in the free condition. Tellurium and selenium also (in the crystalline modification) possess marked metallic appearance; finally, iodine has a metallic luster. The affinity for hydrogen, on the other hand, diminishes with increase in metallic character; the hydrides of iodine, tellurium, antimony, and arsenic are very unstable, and decompose readily into their constituents; finally, germanium, tin, and bismuth do not combine with hydrogen.

The remarkable relations between the atomic weights of the elements of the four groups are noticeable in the following table:

C = 12.00	N = 14.04	O = 16.00	Fl = 19
Si = 28.4	P = 31.00	S = 32.06	Cl = 35.45
Ge = 72	As = 75	Se = 79.1	Br = 79.96
Sn = 118.5	Sb = 120	Te = 127	I = 126.85.

A fuller consideration of these relations will be given in the presentation of the *Periodic System of the Elements*.

THE VALENCE OF THE ELEMENTS. CHEMICAL STRUCTURE OF THE MOLECULES.

Each of the elements of the group of halogens forms but one compound with hydrogen: the halogen hydride. In the case of the elements of the other three groups just considered this simplicity occurs exceptionally. Thus, oxygen and sulphur each form two hydrogen derivatives:

H_2O and H_2O_2; H_2S and H_2S_5.

The hydrides are even more numerous with phosphorus and nitrogen, and with carbon they are almost too numerous to mention. In this confusing multiplicity simple relations can be reached if attention is directed solely to that derivative of the metalloid which contains the most hydrogen—to the compound in which the power of the metalloid to unite with hydrogen attains its maximum. We would then have the following hydrides, which in turn are arranged in groups:

CH_4	NH_3	OH_2	FlH
SiH_4	PH_3	SH_2	ClH
. .	AsH_3	SeH_2	BrH
. .	SbH_3	TeH_2	IH.

Not one of the many hundred combinations of carbon with hydrogen contains more of the latter element than methane; ethane, C_2H_6, follows methane in this respect, but it contains only three atoms of hydrogen to one of carbon, and in all the other hydrides of carbon less even than three atoms of hydrogen are present for each atom of carbon. It must, therefore, be concluded that the carbon atom under the conditions accessible and known to us is not capable of combining with more than four atoms of hydrogen. The same is true of the other elements which have been mentioned. Facts oblige us, therefore, to ascribe a peculiar function of affinity to each element, in its relation to hydrogen, which it does not exceed. This is called its *valence* or *atomicity*. The elements of the fluorine group are univalent; the elements of the oxygen group *bivalent;* nitrogen and its analogues, *trivalent;* carbon and silicon, finally, are *quadrivalent* elements. *The largest number of hydrogen atoms with which one atom of an element can combine determines the valence of the latter.* It has been customary to attribute to the elements, in accordance with their valency, affinity units or valence units, *i. e.*, to say that carbon has four affinity units, oxygen two, etc. This is intended, however, only to indicate that one carbon atom can combine with but four hydrogen atoms, one oxygen atom with but two hydrogen atoms, etc. (see p. 166).

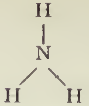
The valence of the elements is frequently designated by lines or Roman numerals placed above the symbols:

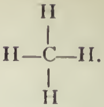
$\overset{\text{I}}{\text{Cl}} \quad \overset{\text{II}}{\text{O}} \quad \overset{\text{III}}{\text{N}} \quad \overset{\text{IV}}{\text{C}}.$

The mutual union of affinity units is indicated by one line:

$H-Cl$
Hydrogen chloride.

$H-O-H$
Water.


Ammonia.

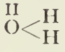


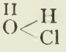
$$\begin{array}{c} H \\ | \\ H-C-H. \\ | \\ H \end{array}$$

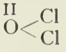
Methane.

In these formulas the atoms of oxygen, of nitrogen, of carbon—indeed, of all the multivalent elements—represent, as it were, the nuclei to which the hydrogen atoms attach themselves.

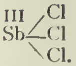
The hydrogen atoms in these molecules can be replaced or substituted by other elements (p. 159). According to this, an atom of each of the univalent halogens can replace one hydrogen atom:


Water.


Hypochlorous acid.


Chlorine oxide.


Nitrogen iodide.


Antimony trichloride.

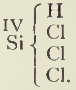
It is more convenient to employ brackets instead of the lines:

$$\overset{IV}{C}\begin{cases} H \\ Cl \\ Cl \\ Cl \end{cases}$$

Chloroform.

$$\overset{IV}{C}\begin{cases} Cl \\ Cl \\ Cl \\ Cl \end{cases}$$

Carbon tetrachloride.



$$\overset{IV}{Si}\begin{cases} H \\ Cl \\ Cl \\ Cl. \end{cases}$$

Silicon chloroform.

By the replacement of hydrogen in the preceding hydrogen compounds by the univalent metal potassium, we obtain

$K-Cl$
Potassium chloride.


Potassium hydroxide.

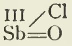
$$\overset{III}{N}\begin{cases} H \\ K \\ K \end{cases}$$

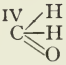
Dipotassium imide.

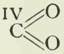
$$\overset{IV}{C}\begin{cases} H \\ H \\ H \\ K. \end{cases}$$

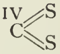
Potassium methide.

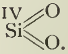
The bivalent elements, like oxygen and sulphur, replace two hydrogen atoms in the compounds of the latter element:


Antimony oxychloride.


Methylene oxide.


Carbon dioxide.


Carbon bisulphide.


Silicon dioxide.

Finally, trivalent nitrogen can replace three atoms of hydrogen, or three of the halogens:

$$\overset{IV}{C}\begin{cases} \overset{III}{N} \\ H \end{cases} \quad \text{or} \quad \overset{I}{H}-\overset{IV}{C}\equiv\overset{III}{N}.$$

Hydrogen cyanide.

$$\overset{IV}{C}\begin{cases} \overset{III}{N} \\ Cl \end{cases} \quad \text{or} \quad \overset{I}{Cl}-\overset{IV}{C}\equiv\overset{III}{N}.$$

Cyanogen chloride.

In these substitutions, in which the elements replace one another atom for atom, we possess a means of determining the molecular weights, previously found from the densities, in a purely chemical manner. Thus, methane, the molecule of which must from its density be represented by CH_4, can have its hydrogen atoms replaced one after the other by chlorine and four compounds, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 result. Analysis has determined their composition. If the molecule of methane were represented by a larger formula, say C_2H_8, then upon chlorination there would result not four but eight different chlorinated methanes: C_2H_7Cl, $C_2H_6Cl_2$, $C_2H_5Cl_3$, etc., of which four (C_2H_7Cl, $C_2H_5Cl_3$, $C_2H_3Cl_5$, C_2HCl_7) would, so far as composition is concerned, differ very decidedly from the preceding. Since, however, never more than four chlorinated methanes have been made, and never one which contained more hydrogen than CH_3Cl or one having less hydrogen than $CHCl_3$, we conclude in a purely chemical way that methane must have the formula CH_4. This method of determining molecular weights can also be applied where the vapor density is not applicable.

These substitutions (replacements) afford a clue to the magnitude of the atomic weights of many elements, in so far as, as has already been repeatedly emphasized, *the atomic weight is the smallest quantity of an element which is present in the molecule of any of its compounds.* If it is found that the smallest quantity by weight of chlorine which enters the molecule of any of its derivatives is to the replaced hydrogen as 35.45 : 1.01 ($O = 16$) then it must be assumed that these numbers represent the atomic weights of the two elements.

Like valence is designated by the word *equivalence.* One atom of chlorine is equivalent to one atom of hydrogen; 35.45 parts, by weight, of chlorine are, then, equivalent to 1.01 parts, by weight, of hydrogen. One atom of oxygen is equivalent to two atoms of hydrogen; consequently, 2.02 parts, by weight, of hydrogen are equivalent to 16.00 parts, by weight, of oxygen, or 1.01 parts of hydrogen to 8 parts of oxygen. Further, one atom of nitrogen, or 14.04 parts, is equivalent to three atoms or 3.03 parts of hydrogen; 1.01 parts of hydrogen is, therefore, equivalent to $\frac{14.04}{3} = 4.68$ parts of nitrogen, etc. These quantities, equal to 8 parts, by weight, of oxygen, are termed *equivalent weights,* and were formerly employed instead of the atomic weights (p. 70). As may be observed from the preceding, the equivalent weights of multivalent elements are parts of the atomic weights which correspond to the valence of the elements.

If, consequently, the valence of the elements, in relation to hydrogen (also to other elements), has a definite value, the question naturally arises—what will result if an atom of hydrogen be withdrawn from the saturated molecules, *e. g.*, water, H_2O, ammonia, NH_3, or methane, CH_4? The resulting *groups* or *residues:*

$-\overset{II}{O}-H$	$-\overset{III}{N}=H_2$	$-\overset{IV}{C}\equiv H_3.$
Hydroxyl.	Amide.	Methyl.

can plainly not exist in a free condition. When set free, these groups, therefore (like the elementary atoms), unite and form saturated molecules. Thus, for example, we obtain the bodies:

$H\overset{II}{O}-\overset{II}{O}H$	$H_2\overset{III}{N}-\overset{III}{N}H_2$	$H_2\overset{III}{P}-\overset{III}{P}H_2$	$H_3\overset{IV}{C}-\overset{IV}{C}H_3.$
Hydrogen peroxide.	Diamide.	Liquid hydrogen phosphide.	Dimethyl or Ethane.

Carbon is particularly inclined to such combination. Upon removing an atom of hydrogen from dimethyl or ethane (C_2H_6) the so-called ethyl group remains:

$$C_2H_5- \quad \text{or} \quad \overset{IV}{C}H_3-\overset{IV}{C}H_2-.$$

in which one carbon affinity is unsaturated; this can again unite with the methyl group, CH_3. The resulting compound would be:

$$C_3H_8 \quad \text{or} \quad \overset{IV}{H_3C}-\overset{IV}{CH_2}-\overset{IV}{CH_3} \quad \text{or} \quad C_2H_5 \,.\, CH_3.$$

By the continuation of this process of a chain-like union, as it were, of the carbon atoms, we obtain a whole series of hydrocarbons (C_4H_{10}, C_5H_{12}, etc.) with the general formula C_nH_{2n+2} (compare page 153).

Not only similar residues or groups, but dissimilar also, combine in this way:

$$\overset{III}{H_2N}-\overset{II}{OH}$$

Hydroxylamine.

$$\overset{IV}{H_3C}-\overset{II}{OH}$$

Methyl hydroxide.

$$\overset{IV}{H_3C}-\overset{III}{NH_2}.$$

Methylamine.

Such combinations are generally effected by reactions of double decomposition. Thus methyl hydroxide (wood-spirit) results from the action of methyl iodide (CH_3I) upon silver hydroxide ($AgOH$):

$$CH_3I + AgOH = CH_3 \,.\, OH + AgI;$$

methylamine by the action of methyl iodide upon ammonia:

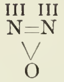
$$CH_3I + NH_3 = CH_3 \,.\, NH_2 + HI.$$

Dimethyl is produced when sodium acts upon methyl iodide:

$$2CH_3I + Na_2 = C_2H_6 + 2NaI.$$

By the withdrawal of iodine by the sodium the methyl groups are liberated, and then combine with each other.

Further, the atoms with several valences can unite with two and three affinities (*double* and *triple* union; there being no intention to assert with what firmness this union exists):



Hyponitrous oxide.

$$\overset{IV}{H_2C}=\overset{IV}{CH_2}$$

Ethylene.

$$\overset{IV}{HC}\equiv\overset{IV}{CH}.$$

Acetylene.

The molecules of elements result by the complete mutual union of their atoms:

$$H-H \qquad O=O \qquad N\equiv N$$

Hydrogen. Oxygen. Nitrogen.

Phosphorus.

This manner of linking or combination of the atoms in the molecule with single affinities is designated *chemical constitution*, or *chemical structure* of compounds; the formulas representing them are called *constitution* or *structural formulas*. Of course, the actual position of the atoms in space (of which we have no knowledge) is not indicated by the chemical structure. The fundamental principle of chemical structure consists in this, that *the affinity unit of one atom unites with the affinity unit of another atom.*

The following circumstances, however, complicate these simple relations: Among the elements of the nitrogen group we saw that phosphorus and antimony combine with 3 and 5 atoms of chlorine and the other halogens; that sulphur, selenium, and tellurium take up 2 and 4 atoms of chlorine and bromine; that iodine unites with 1 and 3 atoms of chlorine and 5 of fluorine. Only the quadrivalent elements, carbon and silicon, are capable of combining with 4 hydrogen atoms, and with not more than 4 of the halogens:

$$\begin{array}{cccc}
\overset{\text{IV}}{CCl_4} & \overset{\text{III}}{PCl_3} & \overset{\text{II}}{SCl_2} & \overset{\text{I}}{ICl} \\
.\,. & \overset{\text{V}}{PCl_5} & \overset{\text{IV}}{SCl_4} & \overset{\text{III}}{ICl_3} \\
.\,. & .\,. & .\,. & \overset{\text{V}}{IFl_5}.
\end{array}$$

Hence it appears that the elements (excepting carbon and silicon) do not express such a constant valence in their relation to chlorine (and to the halogens) as they do to hydrogen. Phosphorus and its analogues appear to be tri- and quinquivalent; the elements of the sulphur group, bi- and quadrivalent; iodine finally appears to be uni-, tri-, and quinquivalent.

The varying valence of the metalloids shows itself more distinctly and frequently in the more stable oxygen derivatives. We are acquainted with the following oxygen compounds of the elements of the four groups already mentioned; the members of each group afford perfectly analogous compounds:

$$\begin{array}{cccc}
\overset{\text{II}}{CO} & \overset{\text{I}}{N_2O} & \overset{\text{III}}{S_2O_3} & \overset{\text{I}}{Cl_2O} \\
\overset{\text{IV}}{CO_2} & \overset{\text{II}}{NO} & \overset{\text{IV}}{SO_2} & \overset{\text{IV}}{ClO_2} \\
.\,. & \overset{\text{III}}{N_2O_3} & \overset{\text{VI}}{SO_3} & \overset{\text{V}}{I_2O_5}. \\
.\,. & \overset{\text{IV}}{NO_2} & \overset{\text{VII}}{S_2O_7} & .\,. \\
.\,. & \overset{\text{V}}{N_2O_5} & .\,. & .\,.
\end{array}$$

The valence of iodine and of nitrogen reaches five, and that of sulphur seven affinity units, assuming that oxygen is constantly bivalent and wholly united to the other element. The elements of the nitrogen group are not more than quinquivalent, both in their relation to the halogens and oxygen:

$$PCl_5,\ PFl_5,\ SbCl_5.$$

Carbon, finally, does not show more than four affinities for hydrogen, chlorine, or oxygen. As we will observe later, these relations are more apparent in the hydroxyl derivatives of the oxides—the acids.

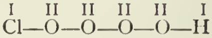
Hence we conclude that *valence is not an absolute property belonging* per se *to and for the elements solely*, but that it is dependent upon the nature of the elements combining with one another and upon the external conditions under which they unite. We can, in general, distinguish two valences: the *hydrogen valence* and the *halogen* or *oxygen valence.* The hydrogen valence is *constant* for all elements; for Cl = 1, for O = 2, for N = 3, for C = 4. The valence of most of the elements appears to be *variable* in respect to oxygen and chlorine. It varies, indeed, as seen from the formulas given above for the chlorine group from 1 to 4 to 5; for the elements of the sulphur group from 4 to 6, and from 3 to 7; for those of the nitrogen group from 1 to 3 to 5, and from 2 to 4.

It is perfectly immaterial whether we ascribe a variable valence to the elements or accept the maximum as the true measure, and regard the lower compounds as *unsaturated*, because we possess no conception of the nature of valence. Later, we will discover that this alteration of valence finds full expression and generalization in the periodic system of the elements, which is based upon the grouping of the elements according to their atomic weights.

From these facts, we have evolved the idea of a *variable valence*. Until recently another opinion prevailed. This, denying the alterability, regards *valence as an absolute constant property of the elementary atoms*. According to this idea, the true valence, or atomicity, is only derivable from the hydrogen compounds; the halogens are absolutely univalent, the elements of the oxygen group bivalent, and those of the nitrogen group trivalent, etc. Different propositions have been made in order to carry out the constant atomicity for all compounds. A chain-like union is assumed in order to explain the oxygen compounds. This is similar to the carbon atoms in the carbon compounds (p. 168). It is represented in the following examples:

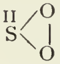
$$\overset{\text{I}}{\text{I}}-\overset{\text{II}}{\text{O}}-\overset{\text{II}}{\text{O}}-\overset{\text{II}}{\text{O}}-\overset{\text{II}}{\text{O}}-\overset{\text{II}}{\text{O}}-\overset{\text{I}}{\text{I}}$$

Iodic anhydride.

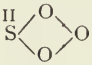


$$\overset{\text{I}}{\text{Cl}}-\overset{\text{II}}{\text{O}}-\overset{\text{II}}{\text{O}}-\overset{\text{II}}{\text{O}}-\overset{\text{II}}{\text{O}}-\overset{\text{I}}{\text{H}}$$

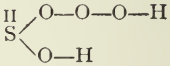
Perchloric acid.



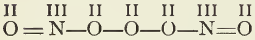
Sulphur dioxide.



Sulphur trioxide.

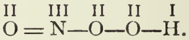


Sulphuric acid.



$$\overset{\text{II}}{\text{O}}=\overset{\text{III}}{\text{N}}-\overset{\text{II}}{\text{O}}-\overset{\text{II}}{\text{O}}-\overset{\text{II}}{\text{O}}-\overset{\text{III}}{\text{N}}=\overset{\text{II}}{\text{O}}$$

Nitrogen pentoxide.



$$\overset{\text{II}}{\text{O}}=\overset{\text{III}}{\text{N}}-\overset{\text{II}}{\text{O}}-\overset{\text{II}}{\text{O}}-\overset{\text{I}}{\text{H}}.$$

Nitric acid.

Hence it would appear that the oxygen atoms can unite without end, in a chain-like manner, similar to the carbon atoms in the carbon compounds. However, a maximum combining affinity of different groups for oxygen does actually occur; this varies regularly from group to group (for iodine = 5, for sulphur = 7, for nitrogen = 5, for carbon = 4). Consider it as we may, on the supposition of constant affinity, the reason for the different number of linking oxygen atoms must be based on the nature of the other element. The fact, then, that the higher oxides or their hydrates ($HClO_4$, H_2SO_4, HNO_3) are more stable than the lower (p. 182), argues decidedly against the chain-like union of the oxygen atoms, which occurs in the unstable peroxides.

To explain the other compounds according to the constant atomicity theory, a difference is conceived between *atomic* and *molecular* compounds. The former are such as can be explained by constant atomicity. All others are regarded as molecular compounds, resulting from the union of two or more molecules, upon the basis of newly acquired molecular affinities. Thus the compounds PCl_5, SCl_4, ICl_3 are viewed as addition products of atomic compounds with chlorine molecules:

PCl_3,Cl_2	SCl_2,Cl_2	ICl,Cl_2.
Phosphorus pentachloride.	Sulphur tetrachloride.	Iodine trichloride.

It was thought that a proof of these bodies being differently constituted from the real atomic compounds was the fact that when vaporized they decomposed into simpler derivatives; the molecular compounds were not regarded as capable of existing as such in the gaseous state. We saw, however, that the decomposition of the molecules PCl_5 and SCl_4 is only gradual, increasing with the temperature, and that they do exist at lower temperatures, undecomposed, in a vapor form (compare p. 141). True atomic compounds, like sulphuric acid and nitric acid, frequently separate into simpler molecules, in their conversion into vapor (compare Sulphuric Acid).

Phosphorus pentafluoride, PFl_5, a gas at ordinary temperatures, is a strong argument in favor of the quinquivalence of phosphorus; iodine, too, forms a volatile pentafluoride, IFl_5. It is noteworthy that, as a general thing, the metalloids yield more stable and higher compounds with the lower halogens (fluorine and chlorine) than with bromine and iodine, which possess higher atomic weights (p. 142). The idea that molecular compounds can also exist in vapor form, would render their distinction from the atomic compounds purely arbitrary—not present in the nature of the bodies themselves. But other gaseous compounds exist, which can, in no light, be regarded as molecular. Thus, the usually quadrivalent or sexivalent tungsten (WCl_6, WBr_6, $WOCl_4$) forms a gaseous pentachloride, WCl_5, and molybdenum, perfectly analogous to tungsten, yields a pentachloride, $MoCl_5$. Further, the quinquivalent vanadium ($VdOCl_3$) yields a gaseous tetrachloride, $VdCl_4$.

The salts of ammonia, according to the theory of constant atomicity, are not regarded as ammonium compounds:

$$\overset{V}{N}H_4Cl,\ \overset{V}{N}H_4NO_3,\ (\overset{V}{N}H_4)_2SO_4$$

(p. 129), but as addition products of ammonia with acids:

$$NH_3,HCl,\quad NH_3,HNO_3,\quad (NH_3)_2,H_2SO_4,$$

which would make the analogy of the same with metallic salts appear rather doubtful. Further, the properties of many compounds like

$$\overset{V}{P}OCl_3,\ (C_2H_5)_3\overset{V}{P}O,\ (CH_3)_3\overset{IV}{S}.OH,\ (CH_3)_2\overset{VI}{S}O,\ (CH_3)_4\overset{V}{N}.OH,$$

and others, cannot be interpreted by the constant valence theory. The existence of potassium permanganate, $KMnO_4$, is not compatible with a constant bi- or quadrivalence of manganese (see p. 178).

Yet, down to the present time, the acceptance of molecular additions could not be entirely dispensed with, especially for the so-called water of crystallization compounds; the proposed effort, however, continues to reduce all such compounds on the basis of higher valence of the elements. While, consequently, the constant valence theory comprises only the so-called atomic compounds, the extended valence idea draws all others into the circle of generalization.

We must, first of all, remember that the nature of chemical union and the cause of the valence of the atoms are entirely unknown to us, and that, therefore, neither the idea of a variable, nor yet of a constant valence constitutes a final explanation. Our task must be restricted rather to representing the varying combination relations of atoms in accordance with the facts and free them as far as possible from hypothetical additions. The supposition of a constant valence, formerly given preference as the simpler, has shown itself to be insufficient. Because it maintains real differences, where such are not perceptible, it departs from the ground of induction. The idea of a variable valence, which takes all facts into consideration, is not prejudicial. It is their simplest expression. Indeed, it finds a pregnant analogy in the deportment of the hydrocarbon radicals. By the elimination of hydrogen from the saturated molecules (C_2H_6, for example), we obtain radicals or groups of increasing valence (C_2H_5, C_2H_4, C_2H_3, C_2H_2). The group C_2H_2, however, is bi- and quadrivalent; the group C_2H_3, uni- and trivalent. It is very probable that the elementary atoms are, like these radicals, of a compound nature.

The principles of chemical structure, just presented, appear most clearly, and with the greatest regularity, with carbon. The constitution of the innumerable varieties of carbon compounds is explained by the quadrivalent nature of the carbon atoms, and their ability to combine with each other by single affinities. In the other, the so-called inorganic compounds, the valence and structure relations are more complicated, and are far less investigated, but even in them so many regularities appear that the actual material is greatly simplified thereby, and is made more comprehensible. The doctrine of valence and structure is the first attempt to refer the facts underlying the law of multiple proportions to the properties of the elementary atoms. As this theory merely comprises actual relations, it cannot be negatived, but only further developed.

The idea of varying valence of the atoms lay undeveloped as the basis of Gerhardt's type theory, according to which chemical compounds were referred to a few fundamental forms or types :

$$\begin{matrix} H \\ H \end{matrix} \qquad \begin{matrix} H \\ Cl \end{matrix} \qquad \begin{matrix} H \\ H \end{matrix}O \qquad \begin{matrix} H \\ H \\ H \end{matrix}N.$$

This mode of comparison will be repeatedly adopted in the following pages (p. 198). After Edward Frankland (1852) had established the doctrine of the saturating capacity of the elementary atoms, August Kekulé added the type CH_4 to those just given and solved in a clear and convincing manner the question how carbon atoms were able to combine with one another and to satisfy their affinities (1857–1859). In this way he developed one of the fundamentals of the chemistry of to-day—*the doctrine of the linking of the atoms.* See the historical sketch in Richter's Organic Chemistry.

OXYGEN COMPOUNDS OF THE METALLOIDS.

Almost all the oxygen derivatives of the metalloids yield acids with water:

$$\underset{\substack{\text{Iodine}\\\text{pentoxide.}}}{I_2O_5} + H_2O = \underset{\substack{\text{Iodic}\\\text{acid.}}}{2HIO_3}; \qquad \underset{\substack{\text{Sulphur}\\\text{trioxide.}}}{SO_3} + H_2O = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4};$$

$$\underset{\substack{\text{Phosphorus}\\\text{pentoxide.}}}{P_2O_5} + 3H_2O = \underset{\substack{\text{Phosphoric}\\\text{acid.}}}{2H_3PO_4}.$$

Conversely, these oxides may be obtained by the removal of water from the acids; therefore, they are ordinarily termed *anhydrides* of the corresponding acids: I_2O_5, anhydride of iodic acid; SO_3, sulphuric anhydride; P_2O_5, phosphoric anhydride, etc.

Salts are formed by the replacement of the hydrogen of the acids by metals. The acids are distinguished as *monobasic*, *dibasic*, *tribasic*, and *polybasic*, depending upon the number of their hydrogen atoms replaceable by metals.

Like the metalloids, the metals possess different valences; the univalent metals (sodium, potassium, silver) each replace *one* hydrogen atom;

those of higher valence replace more. Therefore the metals of higher valence can unite several acid residues. This explains the import, *e. g.*, of the following chemical formulas:

$\overset{(I)_2}{K_2}SO_4$
Potassium sulphate.

$\overset{I}{K}\overset{I}{Na}SO_4$
Potassium-sodium sulphate.

$\overset{II}{Ca}SO_4$
Calcium sulphate.

$\overset{I}{K}NO_3$
Potassium nitrate.

$\overset{II}{Cu}(NO_3)_2$
Copper nitrate.

$\overset{III}{Bi}(NO_3)_3$.
Bismuth nitrate.

The salts of sulphuric acid are called *sulphates*, those of nitric acid, *nitrates*, those of phosphoric acid, *phosphates*, etc. The symbols of the metals are sometimes written at the beginning and sometimes at the end of the chemical formulas of the salts; in the second case we mean to indicate that the metal atoms are in union with the oxygen.

1. OXYGEN COMPOUNDS OF THE HALOGENS.

Oxygen derivatives of fluorine are not known. Iodine is the only one of the remaining halogens which unites directly with oxygen; however, the oxides of chlorine may be prepared by indirect methods. The only known acids of bromine are those corresponding to the oxides.

Chlorine forms the following anhydrides and acids:

ANHYDRIDES.	ACIDS.
Cl_2O	$HClO$, Hypochlorous acid.
. .	($HClO_2$, Chlorous acid.)
ClO_2 or Cl_2O_4	
. .	$HClO_3$, Chloric acid.
. .	$HClO_4$, Perchloric acid.

The compound Cl_2O_4 exists, and must be regarded as a mixed anhydride of chlorous and chloric acids. Chlorous acid itself is not known free, but is stable in the form of salts. Further, the anhydrides of chlorous, chloric and perchloric acids, having the formulas Cl_2O_3, Cl_2O_5 and Cl_2O_7, are not known.

The following formulas express the chemical structure of these compounds:

$\overset{I}{Cl}-\overset{II}{O}-\overset{I}{Cl}$
Hypochlorous anhydride.

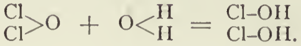
$\overset{I}{Cl}-\overset{II}{O}-\overset{I}{H}$.
Hypochlorous acid.

$O\overset{III}{Cl}-O-\overset{V}{Cl}O_2$
Chlorous-chloric anhydride.

$\overset{V}{Cl}O_2-OH$.
Chloric acid.

$\overset{VII}{Cl}O_3-OH$.
Perchloric acid.

In the acids we assume the presence of the univalent group OH (hydroxyl or water residue) the hydrogen of which can be replaced by metals, through the action of metals or bases. The group (ClO_2 or ClO_3) combined with hydroxyl is called an *acid residue*, or *radical.* In the anhydrides of the monobasic acids two acid radicals are united by an oxygen atom; water converts them into 2 molecules of acid:



$$\begin{matrix}Cl\\Cl\end{matrix}\!>O + O<\!\begin{matrix}H\\H\end{matrix} = \begin{matrix}Cl\text{–}OH\\Cl\text{–}OH.\end{matrix}$$

The salts of perchloric acid are called *perchlorates;* those of chloric acid, *chlorates;* those of chlorous acid, *chlorites;* and those of hypochlorous acid, *hypochlorites.*

Hypochlorous Oxide, Cl_2O (chlorine monoxide, hypochlorous anhydride), is produced by conducting dry chlorine gas over precipitated mercuric oxide, cooled by ice or cold water; the brown oxychloride of mercury is formed at the same time:

$$2HgO + 2Cl_2 = Hg_2OCl_2 + Cl_2O.$$

The precipitated mercuric oxide should be heated to 300° before it is used, otherwise it will be acted upon too energetically by the chlorine, and oxygen instead of hypochlorous oxide will result. Red mercuric oxide is affected too slowly by chlorine.

The disengaged gas is condensed in a bent glass tube, cooled by a freezing mixture of ice and calcium chloride.

It is a reddish-brown liquid, boiling at +5°. In the gaseous condition it has a yellow-brown color, an extremely disagreeable odor, and it attacks the respiratory organs very strongly. The vapor density corresponds to the molecular formula, $Cl_2O = 86.9$. The gaseous or liquid oxide is very unstable and explosive. If heated, or if brought in contact with a flame, or exposed to the action of the electric spark, it decomposes with detonation into oxygen and chlorine:

$$\underset{\text{2 vols.}}{2Cl_2O} = \underset{\text{1 vol.}}{O_2} + \underset{\text{2 vols.}}{2Cl_2}.$$

It is similarly exploded when it is brought in contact with sulphur, phosphorus, and organic substances, such as caoutchouc. It has strong oxidizing and bleaching properties. It dissolves in water to hypochlorous acid:

$$Cl_2O + H_2O = 2HClO.$$

It yields calcium hypochlorite and chlorine when it is conducted over porous calcium chloride:

$$CaCl_2 + 2Cl_2O = Ca(ClO)_2 + 2Cl_2.$$

Hypochlorous Acid, HClO, is only known in aqueous solution. Its presence in chlorine water has been mentioned (p. 52). It is obtained by conducting chlorine into water in which there is suspended freshly precipitated mercuric oxide; the liquid is agitated constantly, while at the same time it is cooled and shut off from the light:

$$HgO + 2Cl_2 + H_2O = HgCl_2 + 2HClO.$$

The mercuric chloride produced combines with the excess of oxide to form oxychloride (see p. 174). After filtration the solution may be distilled; a strong chlorine odor is usually noticeable at the beginning. The first distillates are especially rich in hypochlorous acid. The free chlorine is expelled by blowing air through the solution (Balard).

Hypochlorous acid may be similarly prepared by conducting chlorine into water in which chalk is suspended:

$$CaCO_3 + 2Cl_2 + H_2O = CaCl_2 + CO_2 + 2HClO \text{ (Williamson);}$$

also by the distillation of bleaching lime solutions with as much dilute acid as is required for the decomposition of the hypochlorite, *e. g.:*

$$NaClO + NaCl + HNO_3 = NaNO_3 + NaCl + HClO \text{ (Gay-Lussac).}$$

Boric acid is well adapted for this purpose as it does not decompose the chloride. The concentrated aqueous solutions (5 per cent.) are yellow in color. Upon distillation there ensues a partial decomposition into chloric acid and chlorine:

$$\begin{aligned}(a) \qquad 3HClO &= 2HCl + HClO_3;\\ (b)\ 2HCl + 2HClO &= 2Cl_2 + 2H_2O.\end{aligned}$$

The decomposition is very slight with dilute solutions. These are, unlike the concentrated liquids, quite stable in the light. Their odor is peculiar and they oxidize and bleach energetically. The bleaching action, due to the separation of oxygen *in statu nascendi*, is twice as great as that of free chlorine, as is evident from the following equations:

$$\begin{aligned}Cl_2 + H_2O &= 2HCl + O,\\ 2HClO &= 2HCl + O_2.\end{aligned}$$

Hydrochloric acid decomposes hypochlorous acid into chlorine and water, when just twice as much chlorine is evolved as there is present in the hypochlorous acid.

The acid itself is very feeble, more feeble than carbonic acid, hence it is produced free if chlorine be conducted into aqueous solutions of carbonates:

$$K_2CO_3 + Cl_2 + H_2O = KCl + KHCO_3 + HClO.$$

Its salts (bleaching powder, see Chloride of Lime) are formed together with chlorides by the action of chlorine, in the cold, upon strong bases:

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O.$$

Within certain limits this transposition takes place independently of the temperature and strength of solution if chlorine is not present in excess, otherwise the formation of chlorates will occur even at low temperatures. When the solutions are heated two decompositions of the hypochlorite proceed simultaneously; in one instance chloride and chlorate result:

$$3NaClO = 2NaCl + NaClO_3,$$

and in the other case chloride and oxygen:

$$2NaClO = 2NaCl + O_2.$$

[Compare Foerster and Jorre, Jr. prakt. Ch. 59 (1899), 53 I.]

A hypochlorite is also produced when chlorine is conducted over calcium hydrate powder (see Bleaching Lime).

On shaking the aqueous solution of hypochlorous acid with mercury, there is produced a yellow-brown precipitate of $HgO . HgCl_2$, soluble in hydrochloric acid (salts of hypochlorous acid form HgO). This behavior serves to distinguish hypochlorous acid from chlorine, which under like circumstances forms mercurous chloride, Hg_2Cl_2, insoluble in hydrochloric acid (reaction of Wolters).

Chlorine Trioxide, $Cl_2O_3 = (ClO)_2O$, the anhydride of chlorous acid (p. 131), and the free **Chlorous Acid,** $HClO_2 = ClO.OH$, are unknown. It was formerly supposed that the trioxide resulted by the reduction of chloric acid, if potassium chlorate, $KClO_3$, was decomposed by nitric acid in the presence of reducing substances (arsenic trioxide, sugar and tartaric acid). Later research has, however, shown that in such decompositions it is not the trioxide, but the dioxide, ClO_2, mixed with chlorine and oxygen, which results.

The salts of chlorous acid, the *chlorites, e. g.*, potassium chlorite, are formed by the transposition of the aqueous solution of chlorine dioxide with the alkalies (see below). The *silver salt*, $AgClO_2$, and the *lead salt*, $Pb(ClO_2)_2$, are precipitated from the aqueous solutions of the alkali salts by silver nitrate and lead acetate. They dissolve with difficulty in cold water, and crystallize from hot water in yellowish-green scales. They are decomposed by carbonic acid; the liberated chlorous acid decomposes immediately.

Chlorine Dioxide, ClO_2, or **Chlorine Tetroxide,** Cl_2O_4, formerly called hypochloric acid, is formed when concentrated sulphuric acid acts in the cold upon potassium chlorate. The chloric acid, which first appears, at once decomposes into chlorine dioxide, water, and the stable perchloric acid:

$$3HClO_3 = Cl_2O_4 + HClO_4 + H_2O.$$

It is best obtained (mixed with carbon dioxide) by adding dilute sulphuric acid (with 2 parts of water) to a mixture of potassium chlorate (1 part) and oxalic acid (4.5 parts). Upon the application of a gentle heat a yellow-green gas escapes. It can be condensed by a freezing mixture to a reddish-brown liquid, boiling at 9.9° (under a pressure of 740 mm.), and solidifying at —79°. This liquid may be distilled without decomposition from glass vessels, free from organic matter, if the temperature does not exceed 30°. Violent explosions occur at higher temperatures, so that it is advisable, if proper precautions are not taken, not to pour sulphuric acid upon potassium chlorate. Liquid as well as gaseous chlorine-dioxide is very explosive, especially in contact with organic matter and when heated, but sunlight is without effect.

The formation of the oxide can be effected in a perfectly harmless way, and its powerful oxidizing action be illustrated, by throwing some potassium chlorate and a few pieces of yellow phosphorus into water, contained in a measuring glass, then allowing sulphuric acid to touch the bottom of the tube, drop by drop, by means of a pipette. By the action of the disengaged dioxide the phosphorus will burn under water with a brilliant light.

When concentrated sulphuric acid is added to a mixture of potassium chlorate and sugar, a violent combustion occurs.

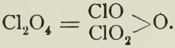
Chlorine dioxide dissolves in water with a yellow color. Alkalies decolorize the solution, forming salts of chloric and chlorous acids:

$$\begin{matrix}ClO\\ClO_2\end{matrix}\!>O + 2KOH = \underset{\text{Potassium chlorite.}}{ClO.OK} + \underset{\text{Potassium chlorate.}}{ClO_2.OK} + H_2O.$$

Sunlight decomposes the aqueous solution of chlorine dioxide into chloric acid, oxygen, and chlorine:

$$3Cl_2O_4 + 2H_2O = 4ClO_2.OH + O_2 + Cl_2.$$

The gas density of the dioxide corresponds to the molecular formula ClO_2. It is, however, very probable that at lower temperatures, in the liquid condition or in aqueous solution, the molecules possess the doubled formula, Cl_2O_4, and that then the compound represents the mixed anhydride of chloric and chlorous acids:



$$Cl_2O_4 = \begin{matrix}ClO\\ClO_2\end{matrix}\!>O.$$

The decomposition of its aqueous solution by alkalies is an argument in favor of this view, as is also its analogy with nitrogen dioxide, NO_2, or nitrogen tetroxide, N_2O_4 (see this), the existence of both of which molecules has been proved.

Chloric Acid, $HClO_3$ or $ClO_2.OH$, is obtained by decomposing an aqueous solution of barium chlorate with sulphuric acid:

$$\underset{\text{Barium chlorate.}}{\overset{''}{Ba}(ClO_3)_2} + H_2SO_4 = \underset{\text{Barium sulphate.}}{\overset{''}{Ba}SO_4} + 2HClO_3.$$

The barium sulphate separates as a white, insoluble powder, and can then be filtered off from the aqueous solution of the acid. This is concentrated without decomposition, under diminished pressure, until the specific gravity becomes 1.28, and it then contains about 40 per cent. of chloric acid; it is oily and, when heated to 40°, decomposes into chlorine, oxygen, and perchloric acid, $HClO_4$. The concentrated aqueous solution oxidizes strongly; sulphur, phosphorus, alcohol, and paper are inflamed by it. Hydrochloric acid eliminates chlorine from the acid and its salts:

$$HClO_3 + 5HCl = 3H_2O + 3Cl_2.$$

The *chlorates* are slowly formed when aqueous hypochlorite solutions are heated; the latter partly break down into oxygen and chlorides. To obtain the chlorate the hypochlorite solution should be slightly supersaturated with chlorine; then the chlorate will form even in the cold but much more rapidly if the solution be heated to 130°. This may be thus explained. The excessive chlorine liberates hypochlorous acid from the hypochlorite:

$$2KClO + 2Cl_2 + 2H_2O = 2KCl + 4HClO,$$

which in turn is rapidly and completely transposed by the hypochlorite into chlorate when chlorine or hydrochloric acid is again liberated:

$$2KClO + 2HClO = KClO_3 + KCl + H_2O + Cl_2,$$

or

$$KClO + 2HClO = KClO_3 + 2HCl;$$

and hypochlorous acid is evolved by the liberated chlorine or hydrochloric acid, etc. The statement previously made that chlorine acting upon cold lyes produces hypochlorites, and chlorates when the solutions are hot, does not harmonize with the facts. The chlorate formation is rapid and complete only when chlorine is in excess (compare Foerster and Jorre). The electrolytic production of chlorates from chlorides will be described in connection with potassium chlorate.

Perchloric Acid, $HClO_4$ or $ClO_3 . OH$. This is the most stable of all the oxygen derivatives of chlorine. Its sodium salt is present in Chile saltpeter. As previously stated, it is produced by the decomposition of chloric acid, but is more easily obtained from its salts. Upon heating potassium chlorate to fusion, oxygen escapes and potassium perchlorate results:

$$2KClO_3 = KClO_4 + KCl + O_2.$$

When this decomposition approaches completion, the fused mass becomes a thick liquid and finally a solid. As potassium perchlorate dissolves with difficulty in water it can be readily separated from the chloride formed simultaneously.

A solution of perchloric acid containing a little sodium chloride, but applicable for all analytical purposes, may be prepared as follows: Commercial sodium chlorate is converted by heat into perchlorate and chloride. Concentrated hydrochloric acid is poured upon the powdered mixture and dissolves almost nothing but perchloric acid:

$$NaClO_4 + HCl = NaCl + HClO_4.$$

The solution is filtered and evaporated until dense white fumes of perchloric acid commence to escape; by distillation under greatly reduced pressure the dihydrate may be obtained [Z. f. anorg. Ch. **9** (1895), 342; **13** (1897), 166].

Roscoe obtained a monohydrate of perchloric acid by distilling potassium perchlorate with four times its quantity of concentrated sulphuric acid until the drops, passing over, no longer solidified. The mass was then heated to 110° until crystals appeared in the neck of the small retort. From this point on *anhydrous perchloric acid* distilled over.

The pure acid is a mobile, colorless liquid, fuming strongly in the air; its specific gravity is 1.78 at 15°. It cannot be preserved even in the dark, since after a few days it decomposes with violent explosion. Heat produces the same result. It also explodes in contact with phosphorus, paper, carbon, and other organic substances. It produces painful wounds when brought in contact with the skin. It absorbs water with avidity, and with one molecule of the same forms the crystalline hydrate $HClO_4 + H_2O$, melting at 50° and passing at 110° into the anhydrous acid and the dihydrate, $HClO_4 + 2H_2O$:

$$2ClO_4H . H_2O = HClO_4 + HClO_4 \quad 2H_2O.$$

The dihydrate may also be obtained by evaporating the aqueous solutions of perchloric and chloric acids. It is a colorless, oily liquid of comparatively great stability. It boils unchanged at 203°. Its specific gravity equals 1.82.

Perchloric acid is also formed at the positive pole by the electrolysis of aqueous solutions of inorganic chlorine compounds; this is due to the liberation of oxygen at the kathode.

Bromine yields the following compounds with oxygen and hydrogen:

$HBrO$, Hypobromous acid.
$HBrO_3$, Bromic acid.
$HBrO_4$, Perbromic acid.

The corresponding anhydrides are not known. The acids are perfectly analogous to the corresponding chlorine compounds.

Hypobromous Acid, $HBrO$, is formed when bromine water acts upon mercuric oxide; the aqueous solution can be distilled *in vacuo*, and possesses properties very similar to those of hypochlorous acid.

Bromic Acid, $HBrO_3$. Bromates are like the chlorates. An aqueous solution of the acid can be obtained from the barium salt by decomposing the latter with sulphuric acid. A more practical method of getting the free acid is to let bromine act upon silver bromate:

$$5AgBrO_3 + 6Br + 3H_2O = 5AgBr + 6HBrO_3,$$

or to oxidize bromine with hypochlorous acid:

$$5Cl_2O + Br_2 + H_2O = 2HBrO_3 + 10Cl.$$

The aqueous solution may be concentrated *in vacuo* until its content reaches 50.6 per cent. $HBrO_3$, and then closely corresponds to the formula $HBrO_3 + 7H_2O$. When heated it decomposes into bromine, oxygen and water. Heat breaks down the alkali bromates into bromide and oxygen without the production of a perbromate.

Perbromic Acid, $HBrO_4$, is said to be formed in the action of bromine vapor upon perchloric acid:

$$HClO_4 + Br = HBrO_4 + Cl,$$

and is perfectly similar to the latter.

Iodine forms the following anhydrides and acids:

I_2O_5	HIO_3	$HIO_4 . 2H_2O$
Iodine pentoxide, Iodic anhydride.	Iodic acid.	Periodic acid (dihydrate).

Iodic Acid, HIO_3. The potassium and sodium salts of this acid occur in Chile saltpeter and are at present the best sources for iodine (see p. 55). The iodates are formed in the same manner as the chlorates and bromates, by dissolving iodine in a hot solution of potassium or sodium hydroxide:

$$6KOH + 3I_2 = 5KI + KIO_3 + 3H_2O.$$

Upon adding barium chloride to this solution sparingly soluble barium iodate separates; it may be transposed by sulphuric acid into insoluble barium sulphate and free iodic acid.

When iodine acts upon cold sodium or potassium hydrate hypoiodites are formed. Schönbein suspected this, but Lonnes proved it:

$$2NaOH + 2I = NaIO + NaI + H_2O.$$

These salts, however, quickly pass into iodates:

$$3NaIO = NaIO_3 + 2NaI.$$

Therefore iodine acts upon hydroxides just like chlorine and bromine, but with iodine the second step of the reaction, the formation of iodate, proceeds very rapidly at the ordinary temperature. The experiments of Binz and also those of Lonnes, however, show that iodine can remain uncombined for quite a time when dissolved in alkaline liquors if potassium iodide be present.

Willgerodt and V. Meyer have prepared organic derivatives of the yet unknown $H - \overset{III}{I} = O$. Indeed, Meyer has made organic, strongly basic compounds which may be derived from *iodonium hydroxide*, $H_2 = \overset{III}{I} - OH$, also unknown. The chemical structure of these derivatives forbids the assumption that iodine is invariably univalent (see Ber. 27 (1894), 426, 1592, and also Richter's Organic Chemistry).

The free acid can be obtained by the oxidation of iodine with strong nitric acid, or by means of chlorine:

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O.$$

Iodates are also produced by the action of iodine upon chlorates or bromates in aqueous solution, whereby the iodine directly eliminates the chlorine and bromine:

$$KClO_3 + I = KIO_3 + Cl.$$

Upon evaporating the aqueous solution the free iodic acid crystallizes in colorless rhombic prisms of specific gravity 4.63. When iodic acid is heated to 170° it decomposes into water and iodic anhydride:

$$2HIO_3 = I_2O_5 + H_2O.$$

It is decomposed, like chloric acid, by hydrochloric acid:

$$2HIO_3 + 10HCl = I_2 + 5Cl_2 + 6H_2O.$$

Reagents, like hydrogen sulphide, H_2S, sulphur dioxide, SO_2, and hydriodic acid, HI, reduce it to iodine:

$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

Iodic Anhydride, I_2O_5, is a white crystalline powder, which dissolves in water to form iodic acid. It decomposes at 300° into iodine and oxygen. It can be obtained directly from ozone and iodine.

Periodic Acid, HIO_4. Normal periodic acid is not known. The hydrate, $HIO_4 . 2H_2O$, is produced by the action of iodine upon perchloric acid:

$$2HClO_4 + I_2 + 4H_2O = 2\,[HIO_4 . 2H_2O] + Cl_2.$$

Upon the evaporation of the aqueous solution, the acid crystallizes in colorless forms, which deliquesce, melt at 130°, and at about 140° decompose into water, oxygen and periodic anhydride:

$$2(HIO_4 . 2H_2O) = I_2O_5 + O_2 + 5H_2O.$$

Periodates result on conducting chlorine into hot alkaline solutions of iodides or iodates. A sodium periodate has been found in Chile saltpeter.

The existence of the hydrates of periodic and perchloric acids as well as of many others (see Sulphuric and Nitric Acids), which were once regarded as molecular compounds, is interpreted at present by the acceptance of hydroxyl groups, directly combined with the element of higher valence:

$$ClO_4H + H_2O = \overset{VII}{Cl}O_2(OH)_3, \text{ Trihydrate or trihydric acid.}$$
$$ClO_4H + 2H_2O = \overset{VII}{Cl}O\,(OH)_5, \text{ Pentahydrate or pentahydric acid.}$$
$$ClO_4H + 3H_2O = \overset{VII}{Cl}(OH)_7, \text{ Heptahydrate or heptahydric acid.}$$

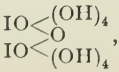
The maximum hydrates, $Cl(OH)_7$ and $I(OH)_7$, in which all seven affinities of the halogen atom are attached to hydroxyl groups, are not known, but probably exist in aqueous solution. As they give up water, and one atom of oxygen becomes simultaneously united with two bonds to the halogen, they yield the lower hydrates—even to the monohydrate $ClO_3 . OH$. Perchloric acid continues monobasic in the polyhydrates, since but *one* hydrogen atom is replaced by metals:

$$ClO_6H_5 + KOH = ClO_4K + 3H_2O.$$

On the other hand, periodic acid ($IO_3 . OH$) is not only monobasic, but as a pentahydrate, $IO(OH)_5 = HIO_4 . 2H_2O$, can, like the polybasic acids, furnish also polymetallic salts, as:

$$\overset{VII}{IO}\left\{\begin{matrix}(OH)_3\\(ONa)_2\end{matrix}\right. \qquad \overset{VII}{IO}\left\{\begin{matrix}(OH)_3\\(OAg)_2\end{matrix}\right. \qquad \overset{VII}{IO}(O.Na)_5 \qquad \overset{VII}{IO}(OAg)_5.$$

Salts also exist which are derived from condensed polyiodic acids, as:



$$\begin{matrix}IO<^{(OH)_4}_{}\\ \quad >O\\ IO<_{(OH)_4}\end{matrix}, \text{ Diperiodic acid, etc.}$$

(Compare Disulphuric Acid, Dichromic Acid, Pyrophosphoric Acid, etc.)

The existence of such salts plainly indicates that the hydrates of acids must be looked upon as hydroxyl compounds, and that iodine and the halogens are, in fact, heptads in their highest combinations.

The oxygen compounds of the halogens in some respects display a character exactly opposite to that of the hydrogen derivatives. While the affinity of the halogens for hydrogen diminishes with increasing atomic weight from fluorine to iodine (see p. 65), the affinity for oxygen is the exact reverse. Fluorine is not capable of combining with oxygen; the chlorine and bromine compounds are very unstable, and are generally not known in free condition; the iodine derivatives, on the contrary, are the most stable. In accord with this is the fact that in the higher oxygen compounds chlorine and bromine are set free by iodine, while in the hydrogen and metallic compounds of the halogens the direct reverse is the case, viz., that iodine and bromine are replaced by chlorine.

Further, the oxygen compounds exhibit the remarkable peculiarity that their stability increases with the addition of oxygen. The lowest acids, HClO, HBrO, are very unstable, even in their salts; they possess a very slight acid character, and are separated from their salts by carbon dioxide. The most energetic and most stable are the highest acids, $HClO_4$, $HBrO_3$, HIO_4, in which the higher valence of the halogens appears. In the sulphur and nitrogen groups those oxides, in which the elements manifest their maximum valence, are the most stable (compare p. 169).

2. OXYGEN COMPOUNDS OF THE ELEMENTS OF THE SULPHUR GROUP.

The elements sulphur, selenium, and tellurium combine with oxygen in several proportions. Sulphur and oxygen form the following derivatives:

S_2O_3
Sulphur
sesquioxide.

SO_2
Sulphur dioxide,
Sulphurous anhydride.

SO_3
Sulphur trioxide,
Sulphuric anhydride.

S_2O_7.
Sulphur heptoxide,
Persulphuric anhydride.

The oxygen derivatives of selenium and tellurium correspond to sulphur di- and trioxides:

SeO_2
Selenium dioxide,
Selenious anhydride.

SeO_3
Selenic
anhydride.

TeO_2
Tellurous
anhydride.

TeO_3.
Telluric
anhydride.

Each of these oxides, sulphur sesquioxide excepted, combines with one molecule of water to form a dibasic acid (p. 172), of which the respective oxide is the anhydride. The acids of sulphur are:

H_2SO_3	H_2SO_4	$H_2S_2O_8$.
Sulphurous acid.	Sulphuric acid.	Persulphuric acid.

By the replacement of one atom of hydrogen by one atom of metal the so-called *acid* or *primary salts* result, while the *neutral* or *secondary salts* are obtained by the replacement of both hydrogen atoms:

$KHSO_4$	K_2SO_4.
Acid potassium sulphate, Monopotassium sulphate.	Neutral potassium sulphate, Dipotassium sulphate.

1. OXYGEN COMPOUNDS OF SULPHUR.

Sulphur combines in four proportions with oxygen. There are in addition nine compounds which contain hydrogen besides these two elements; they are dibasic acids. The only one which can be readily prepared is sulphuric acid. The others are stable only in aqueous solution or in the form of salts. In the table which follows the anhydrides are arranged opposite to the acids into which they pass by the addition of water.

Oxides—Anhydrides.			Acids.	
			Thiosulphuric acid,	$H_2S_2O_3$
			Hyposulphurous acid,	H_2SO_2
Sulphur sesquioxide,	S_2O_3			
Sulphur dioxide,	SO_2		Sulphurous acid,	H_2SO_3
Sulphur trioxide,	SO_3		Sulphuric acid,	H_2SO_4
Sulphur heptoxide,	S_2O_7		Persulphuric acid,	$H_2S_2O_8$
		Polythionic acids	Dithionic acid, (Hyposulphuric acid)	$H_2S_2O_6$
			Trithionic acid,	$H_2S_3O_6$
			Tetrathionic acid,	$H_2S_4O_6$
			Pentathionic acid,	$H_2S_5O_6$.

Both sulphur dioxide and trioxide yield a so-called *anhydro-acid, di-acid* or *pyro-acid:*

$$2SO_2 + H_2O = H_2S_2O_5, \text{ Disulphurous acid.}$$
$$2SO_3 + H_2O = H_2S_2O_7, \text{ Disulphuric acid.}$$

The latter alone is known in a free state.

Sulphur Dioxide, SO_2, or sulphurous anhydride, is formed by burning sulphur or sulphides in the air:

$$S + \underset{\text{1 vol.}}{O_2} = \underset{\text{1 vol.}}{SO_2}.$$

A little trioxide is always produced.

It may also be obtained by heating sulphur with the oxides of copper, manganese and lead:

$$2CuO + 2S = \underset{\substack{\text{Cuprous}\\\text{sulphide.}}}{Cu_2S} + SO_2.$$

It is most conveniently prepared for laboratories by heating concentrated sulphuric acid (1 part) with copper (⅓ part):

$$2H_2SO_4 + Cu = \underset{\text{Copper sulphate.}}{CuSO_4} + SO_2 + 2H_2O.$$

Usually a little cuprous sulphide separates:

$$5Cu + 4H_2SO_4 = Cu_2S + 3CuSO_4 + 4H_2O.$$

This is due to a far-reaching reduction.

Sulphuric acid is similarly decomposed (reduced) by heating it with carbon:

$$2H_2SO_4 + C = 2SO_2 + CO_2 + 2H_2O.$$

By this method we get a mixture of carbon and sulphur dioxides, which are separated with difficulty. A more convenient method for preparing sulphur dioxide consists in allowing ordinary sulphuric acid to act upon calcium sulphite, $CaSO_3$. The latter is mixed with burnt gypsum (⅓ part) and water, then moulded into cubes, which can be introduced into a Kipp generator, as in the preparation of oxygen (p. 81). Owing to its solubility in water, sulphur dioxide must be collected over mercury.

Sulphur dioxide is a colorless gas, with a suffocating odor. One liter of it weighs 2.8615 grams under normal conditions. Its specific gravity equals 2.21 (air = 1) or 64.06 ($O_2 = 32$), corresponding to the molecular formula SO_2. It condenses at —15°, or at ordinary temperatures under a pressure of three atmospheres, to a colorless liquid, of specific gravity 1.43 at 0°, which crystallizes at —76° and boils at —8°. Its critical temperature is 157°; its critical pressure 79 atmospheres. Upon evaporation the liquid sulphur dioxide absorbs much heat; being easily accessible it is used in ice machines. If some of the liquid is poured upon mercury in a clay crucible, and the evaporation accelerated by blowing air upon it, the metal will solidify. Water dissolves 50 volumes of sulphur dioxide gas with liberation of heat. The gas is again set free upon application of heat. The solution shows all the chemical properties of the free gas.

Sulphur dioxide has great affinity for oxygen. The gases combine when dry, if their mixture be conducted over feebly heated platinum sponge;* sulphur trioxide results:

$$\underset{\text{2 vols.}}{2SO_2} + \underset{\text{1 vol.}}{O_2} = 2SO_3.$$

Winkler's method for producing sulphuric acid technically is based on this reaction (compare p. 193).

In aqueous solution the dioxide slowly absorbs oxygen from the air, and becomes sulphuric acid:

$$SO_2 + H_2O + O = H_2SO_4.$$

---

* Instead of platinum sponge, platinized asbestos may be applied; this is obtained by immersing asbestos in a platinic chloride solution, then in ammonium chloride, and afterward drying and igniting.

Aqueous sulphur dioxide is converted more rapidly into sulphuric acid by the action of the halogens chlorine, bromine and iodine:

$$H_2SO_3 + H_2O + Cl_2 = H_2SO_4 + 2HCl.$$

Here the decomposition of a molecule of water is effected in consequence of the affinity of the halogen for hydrogen and of sulphurous acid for oxygen. On adding sulphurous acid to a dark-colored iodine solution the latter is decolorized.

Similarly, sulphurous anhydride and its solution withdraw oxygen from many compounds rich in that element; hence it deoxidizes strongly and passes over into sulphuric acid. Thus chromic acid is reduced to oxide, and the red solution of permanganic acid is decolorized with formation of manganous salts. Many organic coloring substances, like those of flowers, are decolorized by it.* This property is what leads to its application in the bleaching of wools and silks, which are strongly attacked by the ordinary chlorine bleaching agents (p. 53).

Again, the dioxide may be deoxidized by stronger reducing agents (it acts with them as an oxidant); thus in the presence of water, sulphur is separated from it by hydrogen sulphide:

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

If, however, both gases are perfectly dry or strongly diluted by other neutral gases, the action is very slow. (See Hydrosulphurous and Pentathionic Acids.)

A mixture of equal volumes of sulphur dioxide and chlorine unites in direct sunlight to **sulphuryl chloride** SO_2Cl_2 (p. 195). When sulphur dioxide acts upon warmed phosphoric chloride, the products are phosphorus oxychloride, and the compound $SOCl_2$:

$$SO_2 + PCl_5 = POCl_3 + SOCl_2.$$

Chlorthionyl, $SOCl_2$, may be viewed as the chloride of sulphurous acid or as sulphur dioxide in which one atom of oxygen is replaced by two atoms of chlorine (p. 186). Thionyl chloride may be made by the interaction of sulphur dichloride and sulphur trioxide:

$$SO_3 + SCl_2 = SOCl_2 + SO_2$$

[see Michaelis, Ann. Chem. **274** (1894), 184]. It is a colorless liquid with a sharp odor, and boils at 78°. Its specific gravity equals 1.67. Water decomposes it into hydrogen chloride and sulphurous acid:

$$SOCl_2 + H_2O = SO_2 + 2HCl.$$

Sulphurous Acid, H_2SO_3, is not known in free condition, but is probably present in the aqueous solution of sulphur dioxide. On cooling the concentrated solution to 0°, colorless cubical crystals separate, containing probably six molecules of water (Geuther). If the aqueous solution is allowed to stand for some time, especially in sunlight, sulphur separates with the formation of sulphuric acid:

$$3SO_2 + 2H_2O = H_2 2SO_4 + S.$$

---

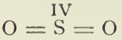
* The acid forms colorless compounds with dyestuffs of the flowers. Dilute sulphuric acid or heat breaks down these derivatives, *i. e.*, the original colors reappear.

Sulphurous acid is dibasic and forms two series of salts; the primary ($KHSO_3$) and secondary (K_2SO_3).

The sulphites, with the exception of those of the alkalies, are insoluble or dissolve with difficulty in water [see Seubert and Elten, Z. f. anorg. Ch. 4 (1893), 44]. When sulphurous acid is separated out from its salts by stronger acids it decomposes into its anhydride and water:

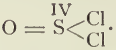
$$Na_2SO_3 + 2HCl = 2NaCl + SO_2 + H_2O.$$

The following is all that is known regarding the chemical structure of sulphurous acid and its derivatives. Its anhydride and chloride have the formulas:



$$O = \overset{\mathrm{IV}}{S} = O$$

and

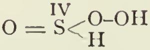


$$O = \overset{\mathrm{IV}}{S}<^{Cl}_{Cl}.$$

By water absorption or by decomposition with water the hydrate

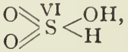
$$O = \overset{\mathrm{IV}}{S}<^{OH}_{OH}$$

results. This formula indicates that the hydrogen atoms or the metals which may replace them are not directly combined with the sulphur, but are linked through oxygen. Organic compounds, esters of sulphurous acid, are known which undoubtedly are derived from this symmetrical formula. The inorganic salts of the acid, however, very probably contain one metal atom in direct union with sulphur, hence their basal acid must have the formula



$$O = \overset{\mathrm{IV}}{S}<^{O-OH}_{H}$$

or



accordingly as sulphur is regarded as quadrivalent or sexivalent. Organic derivatives are also known of this unsymmetrical acid. From this it would appear that the anhydride readily yields compounds which may be derived either from a symmetrical or an unsymmetrical hydrate, SO_3H_2. See Sodium Sulphite and also Richter's Organic Chemistry.

Thermo-chemical Deportment.—Sulphur dioxide is a very powerful exothermic compound. 71.1 Cal. are set free in its formation from rhombic sulphur and oxygen. When it dissolves in much water there is an additional disengagement of 7.7 Cal., so that the heat of formation of the hypothetical sulphurous acid in dilute aqueous solution (from sulphur, oxygen and water) equals 78.8 Cal.:

$$(S,O_2)\text{ gas} = 71.1\text{ ; } (SO_2,Aq) = 7.7\text{ ; } (S,O_2,Aq) = 78.8.$$

In consequence of this great loss of energy the dioxide is a very stable compound; it is only at high temperatures that it sustains a partial separation into sulphur and oxygen.

For its behavior toward oxygen, see p. 187.

Hydrosulphurous Acid, H_2SO_2 or $H_2S_2O_4$. On adding zinc, iron, and some other metals to the aqueous solution of sulphurous acid they dissolve without liberation of hydrogen to yellow-colored liquids. Schönbein (1852) observed that such solutions possessed, when applied to indigo, strong bleaching properties, and assumed that there was in them a peculiar acid, the composition of which was first determined by Schützenberger in 1869. The hydrosulphurous acid is formed there by the action of the hydrogen set free by the zinc upon a second molecule of sulphurous acid:

$$H_2SO_3 + Zn = ZnSO_3 + H_2$$

and

$$H_2SO_3 + H_2 = H_2SO_2 + H_2O.$$

The aqueous solution of the acid has an orange-yellow color, reduces powerfully, bleaches and soon decomposes with separation of sulphur and the formation of sulphurous acid.

The salts are more stable than the acid. The sodium salt is obtained by the action of zinc filings upon a concentrated solution of primary sodium sulphite. It is used in dyeing and cotton printing to bleach indigo. Its composition is not established with certainty; it corresponds to either the formula $NaHSO_2$ or $Na_2S_2O_4$. The salt solutions absorb oxygen very rapidly from the air and change to sulphites.

Sulphur Sesquioxide, S_2O_3, is obtained by the solution of flowers of sulphur in liquid sulphuric anhydride; it separates out in blue drops, which solidify to a mass resembling malachite. It decomposes gradually, more rapidly on warming, into sulphur dioxide and sulphur. It is very violently broken down by water, with formation of sulphur, sulphurous, sulphuric, and polythionic acids. It dissolves with a blue color in fuming sulphuric acid.

Sulphur Trioxide, SO_3, or sulphuric anhydride, is produced, as previously described, by the union of sulphur dioxide and oxygen, aided by heated platinum sponge. Platinized balls of white clay are used in technical operations. It is also formed when sulphur dioxide and air are conducted over ignited oxide of iron, chromic oxide, or manganese oxide. These oxides act like the platinum sponge, platinized asbestos or clay. They are merely contact substances. It can also be made by heating sodium or potassium pyrosulphate (p. 194) and anhydrous sulphates, *e. g.*, ferric sulphate:

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3;$$

and is most conveniently obtained by heating fuming (Nordhausen) sulphuric acid (p. 193); the escaping white fumes are condensed in a chilled receiver. It may be obtained pure by repeated distillation, by fusion at moderate temperature (20–30°), and then pouring it off from the remaining solid portions. It crystallizes in long, broad, transparent needles, which melt at 14.8° to a very mobile liquid. At 16° its specific gravity is 1.940. It distils at 46°. The vapor density agrees with the formula SO_3. The perfectly pure anhydride does not change on preservation. If, however, by absorption of water it contains traces of sulphuric acid, it soon becomes an asbestos-like mass, which does not melt until at about 50°. This was formerly regarded as a peculiar form of sulphuric anhydride. The pure anhydride can be readily obtained from it by distillation [R. Weber; see also Rebs, Ann. Chem. **246** (1888), 379].

Sulphuric oxide fumes strongly in the air, and attracts moisture with avidity. When thrown on water it dissolves with hissing to form sulphuric acid ($SO_3 + H_2O = H_2SO_4$).

When the vapors are led through heated tubes they are decomposed into sulphur dioxide and oxygen.

Thermo-chemical Deportment.—When sulphur dioxide and oxygen combine to form liquid sulphur trioxide 32.1 Cal. are disengaged, so that its heat of formation from the elements is 103.2 Cal.:

$$(SO_2,O) \text{ liquid} = 32.1, \quad (S,O_3) \text{ liquid} = 103.2,$$

inasmuch as the heat of formation of the dioxide = 71.1 Cal. (p. 186). This is another contradiction of Berthelot's principle of the greatest evolution of heat. According to it when sulphur burns in the air or in oxygen it should form not the dioxide but the trioxide, because in the latter case there would occur the greater heat evolution. The fact is that from 91.1–95.5 per cent. of the sulphur is converted into dioxide, and only 2.9–2.5 per cent. into trioxide. In the presence of porous bodies (ferric oxide, etc.) the quantity of trioxide reaches as much as 13 per cent.

On dissolving sulphur trioxide in much water to form aqueous sulphuric acid, 39.2 Cal. are disengaged. The production, therefore, of the aqueous acid from sulphur, oxygen, and water equals (including the heat of formation of SO_3) 142.4 Cal.:

$$(SO_3,Aq) = 39.2; \quad (S,O_3,Aq) = 142.4.$$

If we add to this the heat of formation of water (liquid), 68.3 Cal., the heat of formation of sulphuric acid ($H_2SO_4 = SO_3 + H_2O$) from the elements in dilute aqueous solution will be:

$$(H_2,S,O_4,Aq) = 210.7.$$

The heat of solution of anhydrous sulphuric acid, in much water, equals 17.8 Cal.; hence the heat of formation of anhydrous sulphuric acid from its elements is 210.7 — 17.8 = 192.9:

$$(H_2SO_4,Aq) = 17.8; \quad (H_2,S,O_4) = 192.9.$$

Sulphur Heptoxide, S_2O_7, was obtained by Berthelot on conducting a silent electric discharge of considerable intensity through a mixture of equal volumes of dry sulphur dioxide and oxygen. It separates in oily drops which solidify at 0° to a crystalline mass. This compound must be regarded as the anhydride of persulphuric acid. It decomposes upon standing, immediately when heated, into oxygen and sulphur trioxide:

$$S_2O_7 = 2SO_3 + O.$$

It fumes strongly in the air and with water, as with heat, decomposes into sulphuric acid and oxygen:

$$S_2O_7 + 2H_2O = 2H_2SO_4 + O.$$

Persulphuric Acid, $H_2S_2O_8$, corresponding to sulphuric heptoxide, has not been obtained in a pure condition. A solution of it may be formed at the anode when sulphuric acid (cooled, 40 per cent.) is electrolyzed. Richarz thinks that it is produced in this instance by the sulphuric acid breaking down into the ions H and HSO_4 (p. 92), the latter then combining to $H_2S_2O_8$. Inactive oxygen and ozone are formed simultaneously. A solution of the acid can be obtained by dissolving sulphur heptoxide in dilute sulphuric acid, also by the addition of aqueous hydrogen peroxide to cooled, concentrated sulphuric acid, when ozone is also produced.

The solution of persulphuric acid in sulphuric acid exhibits oxidation reactions similar to those of hydrogen peroxide. It oxidizes ferrous to ferric sulphate, gradually liberates iodine from potassium iodide and decolorizes the blue solution of indigo-sulphuric acid; however, it is not capable of decolorizing a permanganate solution, neither does it oxidize chromic to perchromic acid or affect titanic acid solutions (p. 103).

Hydrogen peroxide is produced if the electrolyzed sulphuric acid contains more than 60 per cent. of sulphuric acid; this is caused by the breaking down of the persulphuric acid which has been formed (p. 101).

The persulphates result in the action of strong bases upon the heptoxide, or, as shown by Hugh Marshall and Berthelot, by the electrolysis of sulphate solutions [Elbs, Jr. prakt. Ch. 48 (1893), 185, and Chem. Zeit. 1895, 1120]. They will be described under the respective metals. Their dilute solutions show the following properties, characteristic for persulphuric acid: when heated they give out ozone, and in the presence of hydrochloric acid chlorine; they precipitate the hydrated dioxide of manganese upon the addition of a manganous salt; in the presence of sulphuric acid they oxidize aniline to aniline black. See p. 198 for the probable structure of persulphuric acid.

SULPHURIC ACID.

H_2SO_4.

It is certain that this acid was known in the fifteenth century, probably long before that time. It is the most important of all the acids; nearly all of them can be prepared directly or indirectly by means of it. In technical chemistry and in the arts it meets with an unusually extensive and varied application, but it is especially valuable, in the Le Blanc soda process, in the refining of petroleum and tar-oils, for the production of aluminium sulphate, blasting material, dyes, artificial manures, etc., etc.

Besides the reactions already mentioned, it is formed in the oxidation of sulphur by nitric acid. It was obtained formerly by heating ferrous sulphate ($FeSO_4$), which breaks down into ferric oxide, sulphurous acid and sulphuric anhydride:

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

At present, however, it is almost exclusively manufactured in large quantities, after the so-called English lead-chamber process. This method is based upon the conversion of sulphur dioxide into sulphuric acid by means of nitric acid. Sulphur, pyrite (FeS_2), or other blendes are roasted in ovens, and the disengaged sulphur dioxide immediately conducted, together with air, into a series of large leaden chambers in which it is frequently brought in contact with nitric acid and steam.

The nitric acid gives up a portion of its oxygen to the sulphur dioxide and thereby oxidizes it in the presence of water to sulphuric acid, which collects on the floors of the lead chambers. The nitrogen oxides, NO, NO_2, and N_2O_3, arising simultaneously from the nitric acid, are capable of transferring, in various ways, the oxygen of the air, which enters the chambers, in the presence of water, to the sulphurous acid so that it passes over into sulphuric acid. As the nitrogen oxides are being constantly regenerated, a given quantity of nitric acid should, according to theory, be capable of converting unlimited amounts of sulphur dioxide into sulphuric acid if the water and oxygen are present in sufficient quantity. Facts show that this is really not true, because a portion of the nitric acid (1–2 parts by weight for 100 parts of sulphurous acid) is reduced to nitrous oxide, nitrogen, and probably ammonia,—compounds which do not participate in the oxidation of the sulphurous acid. Hence, in the lead chambers the nitrogen oxides, particularly nitric oxide, play the rôle of oxygen carriers.

The chemical changes occurring side by side in the lead chambers are influenced by the quantities of the reacting substances and by the temperature; consequently, they are not the same for all chambers, indeed not the same for different parts of the same chamber. The chemical and physical conditions are being constantly altered by the violent mixing together of the gases, and it seems almost a fruitless task to attempt to establish a definite theory for the sulphuric acid manufacture. The most important of these changes appear to be the following:

In the presence of water, the nitric acid oxidizes the sulphur dioxide to sulphuric acid, and the former is reduced to nitric oxide (NO) or nitrogen dioxide (NO_2):

$$3SO_2 + 2HNO_3 + 2H_2O = 3H_2SO_4 + 2NO.$$

The nitric oxide unites with the oxygen of the air (which entered the chambers simultaneously with the sulphur dioxide) to form nitrogen dioxide, which, in the presence of water, converts a fresh portion of sulphur dioxide into sulphuric acid :

$$\mathrm{SO_2 + H_2O + NO_2 = H_2SO_4 + NO.}$$

The regenerated nitric oxide is again subjected to the same transformations. In Lunge's opinion the lead-chamber process is not an alternating reduction and oxidation of the oxides of nitrogen, but rather a condensation of nitric oxide and nitrogen dioxide with sulphur dioxide, oxygen, and water to nitrosylsulphuric acid, $\mathrm{SO_2}{<}\genfrac{}{}{0pt}{}{\mathrm{O\,.\,NO}}{\mathrm{OH}}$ (p. 207) :

$$\mathrm{2SO_2 + 2NO + O_3 + H_2O = 2SO_2}{<}\genfrac{}{}{0pt}{}{\mathrm{O\,.\,NO}}{\mathrm{OH.}}$$

The excess of water in the lead chamber immediately converts this product into sulphuric acid and nitrogen trioxide or a mixture of nitric oxide and nitrogen dioxide :

$$\mathrm{2SO_2}{<}\genfrac{}{}{0pt}{}{\mathrm{O\,.\,NO}}{\mathrm{OH}} + \mathrm{H_2O = 2SO_2}{<}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{OH}} + \mathrm{N_2O_3.}$$

$$\mathrm{N_2O_3 = NO + NO_2;\quad N_2O_3 + H_2O = 2HNO_2.}$$

In the anterior portion of the chamber system the nitrosylsulphuric acid breaks down with the assistance of the sulphurous acid and with the formation of nitric oxide :

$$\mathrm{2SO_2}{<}\genfrac{}{}{0pt}{}{\mathrm{O\,.\,NO}}{\mathrm{OH}} + \mathrm{SO_2 + 2H_2O = 3SO_2(OH)_2 + 2NO.}$$

The regenerated nitric oxide and nitrogen dioxide act together with air and steam upon new quantities of sulphur dioxide in the manner already indicated. According to Lunge, nitrosylsulphuric acid is formed upon the very first action of the nitric acid introduced into the lead chamber :

$$\mathrm{SO_2 + NO_2\,.\,OH = SO_2}{<}\genfrac{}{}{0pt}{}{\mathrm{O\,.\,NO}}{\mathrm{OH,}}$$

and it then reacts in the manner indicated. [See Lunge, Z. f. anorg. Ch. 7 (1894), 212 ; R. Hasenclever, Ber. 29 (1896), III, 2861 ; H. Ost, Lehrbuch des technischen Chemie, 3 Aufl. (1898), and especially Jurisch, in Dammer's Handbuch der chemischen Technologie (1895) I, 163.]

In the lead-chamber process the active nitrogen oxides (NO and NO_2) are carried along and withdrawn from the action by means of the escaping nitrogen and excess of air. To avoid any further loss of nitric acid by this means, the escaping brown gases are conducted through the so-called *Gay-Lussac* tower. This is constructed of lead sheets, and filled with pieces of coke, or, as these are apt to become coated with a mud of lead sulphate which stops them up, with fire-brick or cylinders over which concentrated sulphuric acid constantly trickles. The acid completely absorbs the nitrogen oxides N_2O_3, NO_2 and NO, with formation of nitrosylsulphuric acid (see p. 208). The nitrogen oxides can be regained from the acid—the so-called nitroso-acids—collected at the bottom of the tower, and made useful in the production of sulphuric acid in the chambers. This is effected at present in the so-called *Glover tower*, which is constructed of lead plates and fire-proof bricks, and inserted between the sulphur ovens and lead chambers. In this the nitroso-acid (diluted with the previously obtained chamber acid) is allowed to run over fire-brick, while the hot gases of combustion from the sulphur ovens stream against it. This cools the hot gases to the required temperature (70–80°), water evaporates from the chamber acid, and, at the same time, the nitrogen oxides are set free (see above), and carried into the lead chambers. Hence, the Glover tower serves not only for complete utilization of the nitrogen oxides, but also for the concentration of the chamber acid (to 82 per cent. H_2SO_4).

The chamber process may be illustrated by the following experiment : A large glass flask *A* (Fig. 64) replaces the lead chamber ; in its neck are introduced, by means of a cork, several glass tubes, which serve to introduce the various gases. In *a*, sulphur dioxide is generated by heating a mixture of sulphuric acid and mercury or copper turnings. The flask *b* contains some dilute nitric acid and copper turnings, from which nitric oxide (NO) is evolved. Water is boiled in *c* to get steam. Air enters through *d* while the excess of gases escapes through *e*. By the meeting of nitric oxide (NO) with the air, red fumes of nitrogen dioxide (NO_2) arise, and these in presence of water change the sulphur dioxide to sulphuric acid. The regenerated nitric oxide yields nitrogen dioxide with the oxygen of the air, and converts another portion of sulphur dioxide into sulphuric acid. In time aqueous sulphuric acid collects upon the bottom of the vessel.

If, at first, only sulphur dioxide, nitric oxide and air enter without the steam, we get (by aid of the moisture of the air) the compound $SO_2\left\{\begin{matrix}O.NO\\OH\end{matrix}\right.$ (the so-called nitrosulphuric acid) which covers the walls of the vessel with a white crystalline sublimate. These crystals, known as *lead-chamber crystals*, are also formed in the technical manufacture of sulphuric acid, when an insufficient quantity of steam is conducted into the chambers. Water decomposes them into sulphuric acid and nitrogen oxides.

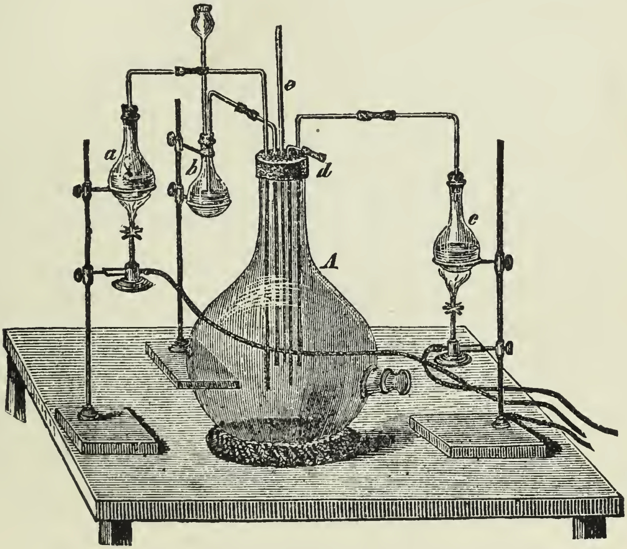


FIG. 64.

The acid collecting in the chambers (chamber acid) possesses, when the operation has been properly conducted, the specific gravity of 1.5 (50° according to Beaumé); it contains about 60 per cent. of sulphuric acid and 40 per cent. of water.* For concentration the chamber acid is first heated in lead pans until the specific gravity reaches 1.71 (60° Beaumé;

---

* The Beaumé araeometer (ἀραιὸς, thin)—hydrometer—used so much in technical work has an empirical scale. For liquids heavier than water an instrument is used the zero point of which is obtained by placing it in pure water. This will give the highest point of the scale. A second fixed point is obtained by dipping the instrument into a solution of 15 parts of salt in 85 parts of water. The distance between the two points is divided into fifteen equal parts or degrees. This division is also continued further downward.

78 per cent. H_2SO_4). The lead pans are strongly attacked by further evaporation. However, in vessels of cast iron, an acid of specific gravity 1.8 (64.2° Beaumé; 86.9 per cent. H_2SO_4) may be obtained. These are the *crude sulphuric acids* (*Acidum sulphuricum crudum*) of commerce. They still contain arsenic, selenium, iron and lead. The purified acid obtained in various ways and diluted is again reduced in lead vessels to 60° Beaumé; further concentration to 65.5–66° Beaumé (92–94 per cent. H_2SO_4; specific gravity 1.83–1.837) is conducted in vessels of glass, porcelain or platinum. The most concentrated acid (98–98.5 per cent. H_2SO_4) is always made in vessels of platinum, which in recent years have been lined within with gold, because they are then less attacked.

By the distillation of the crude English acid an aqueous solution at first distils over (one-third of the distillate), but at 338° we obtain almost pure sulphuric acid (*Acidum sulphuricum purum* or *destillatum*). This has the specific gravity 1.854 at 0° or 1.842 at 12°, and contains about 1.5 per cent. of water. On cooling this to —35° white crystals separate, which after repeated recrystallization melt at 10.5°; this is the *anhydrous* acid, H_2SO_4; also called sulphuric acid monohydrate. The crystalline acid is more readily obtained by cooling the 96–98 per cent. sulphuric acid to 0° or —10°, and then adding already formed crystals. This is the manner in which the anhydrous acid is produced technically; the crystals are separated from the liquid hydrous acid by a centrifugal machine.

Pure anhydrous sulphuric acid, H_2SO_4 (called monohydrate), has the specific gravity 1.8384 at 15° (water of $4° = 1$), and is, therefore, lighter than slightly hydrous acid. When the anhydrous acid is heated, white fumes of sulphur trioxide escape at 40°; the liquid begins to boil at 200°, and at 338° the acid, with 1.5 per cent. of water, again distils over.

From these data it is obvious that sulphuric acid, even at a gentle heat, sustains a partial decomposition (dissociation) into sulphur trioxide and water. The vapor density of sulphuric acid has been found to be 72.0 ($O_2 = 32$) at 332° (near its boiling point). It diminishes at higher temperatures, and is 49 at 416°, where it is constant. This behavior is explained by the dissociation of the acid molecules, according to the equation:

$$\underset{\text{1 vol.}}{H_2SO_4} = \underset{\text{1 vol.}}{SO_3} + \underset{\text{1 vol.}}{H_2O}.$$

Hence the dissociation of the acid is complete at 416°, while it is only about 34 per cent. at 332° (p. 94).

Concentrated sulphuric acid is a thick, oily liquid. On cooling a sulphuric acid, containing about 15 per cent. of water, to 0°, large six-sided prisms of the hydrate $H_2SO_4 + H_2O$ (called sulphuric acid dihydrate) separate; these melt at +8°, and at 205° break down into the anhydrous acid and water. The *second hydrate*, $H_2SO_4 + 2H_2O$, has the specific gravity 1.63, and yields water at 195°. The concentrated acid possesses an extremely great affinity for water, and absorbs aqueous vapor energetically, hence is applied in the drying of gases and in desiccators. It mixes with water with the evolution of considerable heat, and, for this reason, it is especially directed, in diluting the acid, to pour the latter in a thin stream into the water, and not the reverse, as explosive phenomena occur. In mixing sulphuric acid with water, a contraction of the mixture takes place; its maximum corresponds to the hydrate $H_2SO_4 + 2H_2O$ (*i. e.*, 98 parts : 36 parts).

The existence of the hydrates of sulphuric acid is explained, as in the case of periodic acid, by the assumption of hydroxyl groups. Later investigations confirm this idea:

$H_2SO_4 + 2H_2O = S(OH)_6$, Hexahydroxyl sulphuric acid.
$H_2SO_4 + H_2O = SO(OH)_4$, Tetrahydroxyl sulphuric acid.
$H_2SO_4 \quad . \; . = SO_2(OH)_2$, Normal sulphuric acid.

The tetrahydroxyl and the hexahydroxyl sulphuric acids yield only salts of the normal dibasic acid, when they are acted upon by bases. Salts corresponding to the hydrates are not known, as was the case with periodic acid.

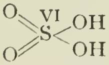
The affinity of sulphuric acid for water is so great that the former withdraws the hydrogen and oxygen from many substances, with the production of water. In addition to carbon, many organic compounds contain hydrogen and oxygen in the proportion in which these elements yield water. The withdrawal of hydrogen and oxygen from such substances leaves the carbon. This explains the charring action of the acid upon wood, sugar, and paper. When sulphuric acid acts upon alcohol (C_2H_6O), ethylene, C_2H_4, results (p. 153).

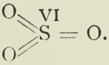
By conducting sulphuric acid vapors over red-hot porous bodies, it is decomposed into sulphur dioxide, water, and oxgen (p. 194):

$$H_2SO_4 = SO_2 + H_2O + O.$$

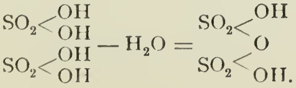
When heated with sulphur, phosphorus, carbon, and some metals (mercury, copper), the acid is reduced to sulphur dioxide (p. 183). Nearly all the metals are dissolved by it, forming salts; only lead, platinum, and a few others are scarcely attacked at all. It is a very strong acid, and, when heated, expels most other acids from their salts; upon this depends its application in the manufacture of hydrochloric, nitric, and many other acids, especially the organic acids. The barium salt ($BaSO_4$) is characterized by its insolubility in water, acids, and alkalies; therefore, sulphuric acid added to solutions of barium compounds produces a white pulverulent precipitate, which serves to detect small quantities of the acid.

The structure of sulphuric acid and its anhydride can, assuming sulphur to be sexivalent, be expressed by the following formulas:





Pyrosulphuric or **Disulphuric Acid**, $H_2S_2O_7$. On withdrawing one molecule of water from two molecules of the acid there results the compound $H_2S_2O_7$, whose formation and structure may be represented by the following formula:



$$\begin{array}{l} SO_2<^{OH}_{OH} \\ SO_2<^{OH}_{OH} \end{array} - H_2O = \begin{array}{l} SO_2<^{OH} \\ \qquad\; O \\ SO_2<_{OH}. \end{array}$$

As this acid contains two hydroxyl groups it is dibasic; yet its manner of formation shows that it possesses an *anhydride* character. Later, we will observe that almost all polybasic acids, like phosphoric acid, $PO(OH)_3$, silicic acid, $SiO(OH)_2$, and chromic acid, $CrO_2(OH)_2$, are capable, by the condensation of several molecules and the elimination of water, of forming like derivatives, which bear the name *Poly-* or *Pyro-acids.* The pyro-acid, corresponding to sulphurous acid, is also known in salts.

The disulphuric acid is contained in the so-called *fuming* or *Nordhausen sulphuric acid* (*Acidum sulphuricum fumans*, oil of vitriol), which was formerly obtained by heating dehydrated ferrous sulphate—green vitriol ($FeSO_4$). It is a thick, oily, strongly fuming liquid, of specific gravity 1.86–1.9. When it is cooled, large colorless crystals of disulphuric acid ($H_2S_2O_7$) separate; these melt at 35°. Heat breaks it down into sulphuric acid and sulphur trioxide, which volatilizes:

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$

Conversely, disulphuric acid may be obtained by dissolving sulphur trioxide in sulphuric acid:

$$H_2SO_4 + SO_3 = H_2S_2O_7.$$

The production of fuming sulphuric acid also depends on this, as it may be regarded as a solution of sulphur trioxide or pyrosulphuric acid in an excess of sulphuric acid.

Technically, fuming sulphuric acid is obtained from pyrites (FeS_2)—(at present only in Bohemia). The decomposition of the pyrites in the air yields ferrous sulphate and ferric sulphate, which can be dissolved out with water. The solution is evaporated, and the residue roasted in a reverberatory furnace, whereby the ferrous salt is changed to ferric salt. The latter is then distilled from earthen retorts, when sulphuric acid and sulphur trioxide pass over and are collected in the receivers:

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

$$Fe\left\{\begin{matrix}(SO_4)_2\\(OH)_2\end{matrix}\right. = Fe_2O_3 + SO_3 + H_2SO_4.$$

The residue, consisting of red ferric oxide, finds application as colcothar (*caput mortuum*) in polishing and as a paint.

Solid, crystalline pyrosulphuric acid has been recently introduced into the market as a substitute for the fuming liquid sulphuric acid. It is made by conducting the theoretical amount of sulphur trioxide into concentrated sulphuric acid (see above). Sulphur trioxide is prepared by two distinct methods at present.

In Winkler's method sulphuric acid of 66° Baumé is first allowed to run into retorts raised to a red heat. The mixed gases, sulphur dioxide, oxygen and water (p. 193), resulting from this action, are freed from steam by passing through a coke tower through which trickles concentrated sulphuric acid. The dry mixture is then conducted over heated platinized balls of white clay and the resulting sulphur trioxide is collected in concentrated sulphuric acid.

The more recent method of Wolters consists in producing sodium pyrosulphate by heating sodium sulphate with concentrated sulphuric acid:

$$\underset{\text{Sodium sulphate.}}{Na_2SO_4} + H_2SO_4 = \underset{\text{Sodium pyrosulphate.}}{Na_2S_2O_7} + H_2O.$$

An intermediate product in this reaction is primary sodium sulphate—$NaHSO_4$—which upon the application of heat gives up water and passes into the pyrosulphate. By the action of concentrated sulphuric acid upon the latter the anhydride is liberated and distilled off in a vacuum:

$$Na_2S_2O_7 + H_2SO_4 = 2NaHSO_4 + SO_3.$$

The residual sodium sulphate can again be converted into pyrosulphate. Sodium pyrosulphate decomposes at about 600° into sodium sulphate and sulphur trioxide, thus:

$$Na_2S_2O_7 = Na_2SO_4 + SO_3.$$

Sulphuric Acid Chloranhydrides.—Under the name of halogen anhydrides we understand the derivatives resulting from the replacement of hydroxyl in acids by chlorine. Conversely, the chloranhydrides, by the action of water, pass into the corresponding acids:

$$SO_2{<}^{Cl}_{Cl} + 2H_2O = SO_2{<}^{OH}_{OH} + 2HCl.$$

The ordinary method for the preparation of the chloranhydrides consists in permitting phosphorus pentachloride to act on the acids. Sulphuric acid has two hydroxyl groups; therefore it can furnish two chloranhydrides.

The *first*, $SO_2{<}^{Cl}_{HO}$, *Sulphuryl Hydroxy-chloride*, or *Chlorsulphonic Acid*, results when one molecule of phosphorus pentachloride acts upon one molecule of sulphuric acid:

$$SO_2{<}^{OH}_{OH} + PCl_5 = SO_2{<}^{Cl}_{OH} + POCl_3 + HCl.$$

The resulting oxychloride of phosphorus acts upon two additional molecules of sulphuric acid, with formation of metaphosphoric, hydrochloric, and chlorsulphonic acids:

$$2SO_2(OH)_2 + POCl_3 = 2SO_2{<}^{Cl}_{OH} + HPO_3 + HCl.$$

It is formed, too, by the direct union of sulphuric anhydride with hydrochloric acid:

$$SO_3 + HCl = SO_3ClH.$$

The most practical method for its formation consists in conducting chlorine gas through sulphuric acid (15 parts), and gradually adding phosphorus trichloride (7 parts). Or, hydrochloric acid gas is led into solid fuming sulphuric acid ($H_2S_2O_7$), as long as absorption occurs, and then the acid is distilled (Otto).

Chlorsulphonic acid is a colorless, strongly fuming liquid, of specific gravity 1.716 at 18°, and boils without decomposition at 152°. The salt $SO_2{<}^{Cl}_{OK}$ results from the union of sulphur trioxide with potassium chloride.

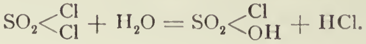
The *second* chloranhydride, SO_2Cl_2, or *Sulphuryl Chloride*,* forms when phosphorus pentachloride acts upon sulphuric anhydride; and also by the direct union of sulphur dioxide with chlorine in sunlight:

$$\underset{1\ \text{vol.}}{SO_2} + \underset{1\ \text{vol.}}{Cl_2} = \underset{1\ \text{vol.}}{SO_2Cl_2}.$$

---

* The group SO_2 combined with 2OH-groups in sulphuric acid, is known as *Sulphuryl.*

The most convenient method for its formation is to pass equal volumes of sulphur dioxide and chlorine gas into a capacious flask, containing some camphor, which causes the union of the gases to form sulphuryl chloride. A colorless, suffocating, strongly fuming liquid, of specific gravity 1.667 at 20° (referred to water at 4°), results. It boils at 69.1°. Water decomposes it slowly at the ordinary temperature into sulphuric and hydrochloric acids. A little water will first change it to chlorsulphonic acid:

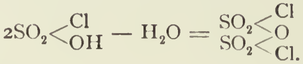


$$SO_2{<}\begin{matrix}Cl\\Cl\end{matrix} + H_2O = SO_2{<}\begin{matrix}Cl\\OH\end{matrix} + HCl.$$

Its vapor density is normal at 130°; at higher temperatures it breaks down into sulphur dioxide and chlorine:

$$SO_2Cl_2 = SO_2 + Cl_2.$$

Pyrosulphuryl Chloride, $S_2O_5Cl_2$, is the chloranhydride of pyrosulphuric acid. It is obtained by several reactions, chiefly, however, by the action of phosphorus pentachloride or phosphorus pentoxide upon chlorsulphonic acid:



$$2SO_2{<}\begin{matrix}Cl\\OH\end{matrix} - H_2O = \begin{matrix}SO_2{<}^{Cl}\\ \quad {>}O\\ SO_2{<}_{Cl.}\end{matrix}$$

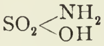
It is a thick liquid, fuming in the air; has a specific gravity of 1.819 at 18°, and boils at 142°. At 210° it shows a normal density; it is dissociated at higher temperatures, corresponding to the equation:

$$S_2O_5Cl_2 = SO_3 + SO_2 + Cl_2.$$

It dissolves gradually in water, without hissing, and decomposes into sulphuric acid and hydrochloric acid; at first, with a little water it yields chlorsulphonic acid.

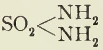
AMIDO-DERIVATIVES OF SULPHURIC ACID.

The amide of an acid is produced when its hydroxyl is replaced by the univalent group NH_2. In the case of polybasic acids there are several amides as there are several chlorides, depending upon whether the hydroxyl groups are partly or completely replaced by amido-groups. Sulphuric acid yields:



$$SO_2{<}\begin{matrix}NH_2\\OH\end{matrix}$$

Amidosulphonic acid,
Sulphanilic acid
or Amidosulphuric acid.



$$SO_2{<}\begin{matrix}NH_2\\NH_2\end{matrix}$$

Sulphamide,
Sulphuric acid amide.

They may be obtained by treating the corresponding chlorides with dry ammonia.

Sulphamide, formed by Traube on conducting ammonia into a solution of sulphuric acid chloride:

$$SO_2Cl_2 + 4NH_3 = SO_2(NH_2)_2 + 2NH_4Cl,$$

consists of large, colorless crystals melting at 81°. It dissolves readily in water; its solution is neutral in reaction and has a slightly bitter taste. Alkalies and acids partly saponify it in aqueous solution, forming at first sulphamic acid, then sulphuric acid and ammonia—a reaction corresponding to the decomposition of the chlorides of sulphuric acid by water. Sulphamide, like sulphuric acid, contains two hydrogen atoms replaceable by metals. It yields a silver salt of the composition $SO_2(NHAg)_2$ [see W. Traube, Ber. 26 (1893), 1, 607].

In the action of ammonia upon sulphuryl chloride, *sulphimide*, $(SO_2) = NH$, is produced together with sulphamide. It is also formed when the latter is heated to 200–210°. It acts like a monobasic acid; its salts, *e. g.*,

$$SO_2N . K, \quad SO_2N . Na, \quad (SO_2N)_2Ba + 2H_2O,$$

are readily soluble in water and crystallize well. Crystallized sulphimide is not yet known; by the absorption of water it passes readily into sulphuric acid and ammonia (W. Traube).

In addition to the preceding there are other compounds derived either from ammonia or from hydroxylamine in such manner that the hydrogen in them in direct union with nitrogen is replaced by the univalent sulpho-group—SO_3H. Two series result:

$NH_2 . SO_3H$ Amidosulphuric acid (see p. 196).	$HO . NH . SO_3H$ Hydroxylamine sulphonic acid.
$NH(SO_3H)_2$ Imidosulphonic acid, Disulphamic acid.	$HO . N(SO_3H)_2$. Hydroxylamine disulphonic acid.
$N(SO_3H)_3$ Nitrolosulphonic acid, Trisulphamic acid.	

The acids of the first series are obtained from ammonia and sulphur trioxide or chlorsulphonic acid; also, just like the second, from sulphurous acid and nitrous acid or hydroxylamine in aqueous solution [Raschig, Ann. Chem. **241** (1887), 161; also Chem. Centralblatt, 1897, I, 10; compare p. 131].

Thiosulphuric Acid, $H_2S_2O_3 = SO_2<^{OH}_{SH}$, generally known as *hyposulphurous acid*, can be considered as sulphuric acid in which the oxygen of an hydroxyl group is replaced by sulphur. It is not known in a free condition, since as soon as it is liberated from its salts by stronger acids it at once decomposes into sulphur dioxide, sulphur and water (compare Ber. **22** (1889), 1686, 2703):

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O.$$

Its salts, called *hyposulphites*, are of practical importance (compare Sodium Hyposulphite). They are formed by the direct addition of sulphur to sulphites:

$$Na_2SO_3 + S = Na_2S_2O_3;$$

similar to the formation of sulphates by the addition of oxygen to the sulphites.

The formation of its sodium salt by the action of iodine upon a mixture of sodium sulphite and sodium sulphide,

$$NaSNa + NaSO_3 . Na + I_2 = \underset{\text{Sodium hyposulphite.}}{NaS . SO_3Na} + 2NaI,$$

is taken as evidence of the chemical structure of the acid (Spring). However, this reaction can take place in two phases:

$$1.\ Na_2S + I_2 = 2NaI + S; \quad 2.\ S + Na_2SO_3 = Na_2S_2O_3.$$

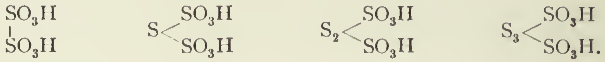
Sodium amalgam resolves sodium hyposulphite into sodium sulphite and sodium sulphide.

POLYTHIONIC ACIDS.

By this name (from πολὺς, many, and θεῖον, sulphur) are understood the acids of sulphur, containing two or more atoms of the latter with six oxygen atoms and two hydrogen atoms. Salts of the following are known:

$H_2S_2O_6$, Dithionic acid.
$H_2S_3O_6$, Trithionic acid.
$H_2S_4O_6$, Tetrathionic acid.
$H_2S_5O_6$, Pentathionic acid.

Following Blomstrand and Mendelejeff it may be assumed that there are two univalent groups—SO_3H or $\overset{VI}{SO_2}.OH$—in these acids which in dithionic acid are directly combined, but in the other acids are joined through S, S_2, S_3, with one another.



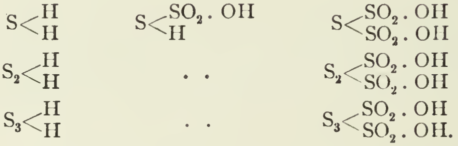
$$\begin{array}{l}SO_3H\\ |\\ SO_3H\end{array} \qquad S<\begin{array}{l}SO_3H\\SO_3H\end{array} \qquad S_2<\begin{array}{l}SO_3H\\SO_3H\end{array} \qquad S_3<\begin{array}{l}SO_3H\\SO_3H.\end{array}$$

The group $\overset{VI}{SO_3H}$ is known as the *sulpho*-group; it is also present in organic sulpho-acids, and corresponds to the acid-forming carbon group, COOH, called *carboxyl.* From this group are derived the acids just mentioned:

$$H.SO_2.OH \qquad HO.SO_2.OH \qquad O<\begin{array}{l}SO_2.OH\\SO_2.OH\end{array} \qquad HS.SO_2.OH.$$

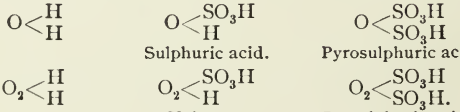
Sulphurous acid. Sulphuric acid. Pyrosulphuric acid. Thiosulphuric acid.

The formulas of the polythionic acids may also be derived from the formulas of the hydrogen sulphides, H_2S, H_2S_2, and H_2S_3, if the hydrogen atoms in these be replaced by the sulpho-group. If in the case of the ordinary hydrogen sulphide this replacement extends merely to one hydrogen atom, thiosulphuric acid results; the acids corresponding to it are not known in the other two series:



$$\begin{array}{lll} S<\begin{array}{l}H\\H\end{array} & S<\begin{array}{l}SO_2.OH\\H\end{array} & S<\begin{array}{l}SO_2.OH\\SO_2.OH\end{array}\\ S_2<\begin{array}{l}H\\H\end{array} & .\ . & S_2<\begin{array}{l}SO_2.OH\\SO_2.OH\end{array}\\ S_3<\begin{array}{l}H\\H\end{array} & .\ . & S_3<\begin{array}{l}SO_2.OH\\SO_2.OH.\end{array}\end{array}$$

Similarly, sulphuric acid and pyrosulphuric acid are derived from water; whereas persulphuric acid must, according to Michaelis and Richarz, be referred to hydrogen peroxide:



$$\begin{array}{lll} O<\begin{array}{l}H\\H\end{array} & O<\begin{array}{l}SO_3H\\H\end{array} & O<\begin{array}{l}SO_3H\\SO_3H\end{array}\\ O_2<\begin{array}{l}H\\H\end{array} & O_2<\begin{array}{l}SO_3H\\H\end{array} & O_2<\begin{array}{l}SO_3H\\SO_3H.\end{array}\end{array}$$

Sulphuric acid. Pyrosulphuric acid.
Unknown. Persulphuric acid.

This is an example of the type idea mentioned on p. 172. Whether the formulas deduced above actually represent the true chemical structure of the polythionic acids is at present very questionable [see Debus, Ann. Chem. 244 (1888), 181].

Dithionic Acid, $H_2S_2O_6$, is only known in aqueous solution. When concentrated *in vacuo* or when heated it decomposes into sulphuric acid and sulphur dioxide. Its manganese salt (together with manganous sulphate) results from the action of sulphur dioxide upon manganese dioxide (MnO_2) suspended in water:

$$MnO_2 + 2SO_2 = MnS_2O_6$$

and

$$MnO_2 + SO_2 = MnSO_4.$$

Barium hydroxide converts this into the barium salt, from which the free dithionic acid in aqueous solution is obtained by means of sulphuric acid.

Trithionic Acid, $H_2S_3O_6$, is not known in a free condition. Its salts are produced when an aqueous solution of primary potassium sulphite is digested with flowers of sulphur:

$$6KHSO_3 + 2S = 2K_2S_3O_6 + K_2S_2O_3 + 3H_2O.$$

Separated from its salts by other acids it decomposes rapidly into sulphuric acid, sulphur dioxide, and sulphur. Its production by the action of iodine upon a mixture of sodium sulphite and hyposulphite is especially interesting:

$$Na_2S_2O_3 + Na_2SO_3 + I_2 = Na_2S_3O_6 + 2NaI.$$

It is also formed from sulphur dichloride and sodium sulphite:

$$SCl_2 + 2Na_2SO_3 = Na_2S_3O_6 + 2NaCl \text{ (Spring)}.$$

The tri- and not a tetrathionate is produced when sulphur dichloride is used.

Tetrathionic Acid, $H_2S_4O_6$. Its salts are produced when iodine acts upon solutions of the hyposulphites:

$$2KS.SO_3K + I_2 = \underset{\text{Potassium tetrathionate.}}{K_2S_4O_6} + 2KI.$$

This reaction is applied in volumetric analysis for the quantitative determination of iodine, and such substances as separate iodine from potassium iodide (see Sodium Thiosulphate).

The tetrathionic acid, separated from its salts by stronger acids, is very unstable, and when its aqueous solution is concentrated it decomposes into sulphuric acid, sulphur dioxide, and sulphur. An aqueous solution of the acid can be easily prepared by conducting hydrogen sulphide into aqueous sulphurous acid:

$$4SO_2 + 3H_2S = H_2S_4O_6 + 2H_2O + 3S.$$

If the solution be saturated with bases, neutral and acid tetrathionates result, *e. g.*,

$$BaS_4O_6 + 2H_2O \text{ and } Zn(HS_4O_6)_2.$$

Pentathionic Acid, $H_2S_5O_6$, is supposed to be produced together with tetrathionic acid when hydrogen sulphide acts upon aqueous sulphurous acid:

$$5H_2S + 5SO_2 = H_2S_5O_6 + 4H_2O + 5S$$

(Wackenroder's liquid; the dry gases do not react). It was from this solution that Debus first prepared pure, crystallized pentathionates.

All the polythionic acids are distinguished from sulphuric acid by the solubility of their barium salts. The alkali salts of pentathionic acid decompose in aqueous solution in such a manner that after some time the salts of the other polythionic acids are also present in the solution.

---

2. OXYGEN DERIVATIVES OF SELENIUM AND TELLURIUM.

SeO_2 Selenium dioxide.	H_2SeO_3 Selenious acid.
. . .	H_2SeO_4. Selenic acid.

Selenium Dioxide, SeO_2, or selenious anhydride, is produced when selenium burns in the air or in oxygen. It consists of long white needles, which sublime at about 320° without fusing. It dissolves readily in water, forming **selenious acid,** H_2SeO_3. The latter is also obtained by dissolving the metal in concentrated nitric acid. When the solution is evaporated it crystallizes in large, colorless prisms, which decompose, on heating, into the anhydride and water. Sulphurous oxide reduces selenious acid, with separation of free selenium:

$$H_2SeO_3 + 2SO_2 + H_2O = 2H_2SO_4 + Se.$$

It is similarly reduced by potassium iodide in hydrochloric acid solution with the simultaneous separation of iodine:

$$SeO_2 + 4KI + 4HCl = 4KCl + 2H_2O + Se + 2I_2.$$

Selenic Acid, H_2SeO_4, is obtained by conducting chlorine gas into an aqueous solution of selenious acid:

$$H_2SeO_3 + H_2O + Cl_2 = H_2SeO_4 + 2HCl.$$

The solution may be concentrated until it attains a specific gravity of 2.6 when it becomes an oily liquid, similar to sulphuric acid, and contains 95 per cent. of selenic acid, H_2SeO_4. If the solution be heated above 260°, the acid breaks down into selenium dioxide, oxygen and water. It was from this solution that Cameron and Macallan obtained the pure acid as a crystalline mass, melting at 58°. It forms a hydrate with water, $H_2SeO_4 . H_2O$, melting at 25°. Its anhydride is not known.

The salts of selenic acid are known as *selenates*, those of selenious acid as *selenites* [see Jahr. Chem. 1889, 388].

The derivatives of tellurium are very similar to those of selenium.

Tellurium Dioxide, TeO_2, results when tellurium is burned, and forms a white crystalline mass, fusing at a red heat and subliming. It is almost insoluble in water.

Tellurous Acid, H_2TeO_3, is produced when the metal is dissolved in concentrated nitric acid. Water will precipitate it from such a solution in the form of a white amorphous powder. On warming, it readily decomposes into the dioxide and water.

Telluric Acid, H_2TeO_4. Potassium tellurate is produced when tellurium or its dioxide is fused with saltpeter. Tellurium is added to an excess of dilute nitric acid in which it dissolves with violent reaction. The resulting dioxide is oxidized by means of a little more than the calculated quantity of chromic acid:

$$3TeO_2 + 2CrO_3 + 3H_2O = 3H_2TeO_4 + Cr_2O_3.$$

The greater portion of the telluric acid separates on evaporation. It is purified by precipitation with concentrated nitric acid from its aqueous solution [Z. f. anorg. Ch. x (1895), 190]. The acid crystallizes from its aqueous solution with two molecules of water ($H_2TeO_4 + 2H_2O$) in isometric or triclinic forms, which at 100° lose all their water and break down into a white powder of telluric acid, H_2TeO_4. The latter is not very soluble in water, and manifests a slight acid reaction. When carefully heated, telluric acid breaks down into water, and the trioxide, TeO_3, which is a yellow mass insoluble in water, and by further application of heat decomposes into the dioxide and oxygen.

3. OXYGEN DERIVATIVES OF THE ELEMENTS OF THE NITROGEN GROUP.

The halogens combine with one atom of hydrogen to form halogen hydrides; their oxygen acids also containing one atom of hydrogen.

The elements of the sulphur group contain two atoms of hydrogen in their hydrogen derivatives and oxygen acids. Accordingly, we find that the elements of the nitrogen group combine with three atoms of hydrogen, and form acids which also contain three atoms of the same element:

HCl	H_2S	PH_3
$HClO_3$	H_2SO_3	PO_3H_3
$HClO_4$	H_2SO_4	PO_4H_3.

The acids of the nitrogen group containing three atoms of hydrogen, designated *normal* or *ortho-acids* (ὀρθός, correct, real, true), as H_3PO_4, H_3AsO_4, H_3AsO_3, can yield monobasic acids by the removal of one molecule of water. Such derivatives, having one atom of hydrogen, are called *meta-acids* (μετὰ, a word which here expresses a change in condition):

H_3PO_4 Orthophosphoric acid.	HPO_3 Metaphosphoric acid.
Na_3AsO_3 Sodium orthoarseniate.	$NaAsO_2$. Sodium meta-arseniate.

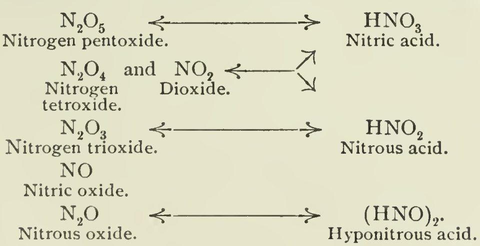
These meta-acids of phosphorus pass into the ortho-acids by the absorption of water. The ortho-acids of nitrogen, on the other hand, are less stable and only exist in some salts. The ordinary acids and salts of nitrogen belong to the meta-series and contain one atom of hydrogen (or metal):

(H_3NO_4) Orthonitric acid.	HNO_3 Ord. Nitric acid.
(H_3NO_3) Orthonitrous acid.	HNO_2. Ord. Nitrous acid.

The further exit of water produces the true anhydrides (p. 183).

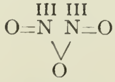
---

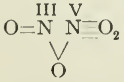
1. OXYGEN DERIVATIVES OF NITROGEN.

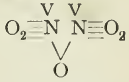


The following formulas express the structure of these compounds:


Nitrous oxide.


Nitrogen trioxide.


Nitric-nitrous anhydride (tetroxide).


Nitrogen pentoxide.

$HO-\overset{III}{N}=\overset{III}{N}-OH$
Hyponitrous acid.

$O=\overset{III}{N}-OH$
Nitrous acid.

$O_2\equiv\overset{V}{N}-OH$.
Nitric acid.

The salts of nitric acid are called *nitrates;* those of nitrous acid, *nitrites.*

NITRIC ACID.

HNO_3.

This acid occurs in nature only in the form of salts,—potassium, sodium, and calcium nitrates (compare these),—which have resulted from the decay of nitrogenous organic substances in the presence of strong bases (the alkalies) and Bacillus nitrificans. It is sometimes present in the air as ammonium salt. The free acid is formed in very slight quantity by conducting electric sparks through moist air; most readily with a mixture of 5 volumes of air and 6 volumes of oxygen, which may obtain technical value if the electricity and oxygen can be prepared cheaply enough. At present Chile saltpeter is the principal source of nitric acid.

To prepare nitric acid heat potassium or sodium nitrate in a retort with sulphuric acid, when the nitric acid will distil over and acid sodium or potassium sulphate remain:

$$NaNO_3 + H_2SO_4 = HNaSO_4 + HNO_3.$$

If one molecule of sulphuric acid be used with two molecules of the nitrate, the resulting acid sulphate will at higher temperatures act upon the second molecule of nitrate in the sense of the equation:

$$NaHSO_4 + NaNO_3 = HNO_3 + Na_2SO_4.$$

The temperature requisite to complete the reaction is, however, so high that a portion of the nitric acid will be decomposed.

Perfectly anhydrous nitric acid has not yet been obtained. The most concentrated acid (99.8 per cent. HNO_3) is a colorless liquid of specific gravity 1.56 at 0°; it fumes in the air, and at —47° solidifies to a crystalline mass. At ordinary temperatures it undergoes a partial decomposition (similar to sulphuric acid) into water, oxygen, and nitrogen dioxide, NO_2, which dissolves in the acid, with a yellowish-brown color; the colorless acid therefore becomes colored upon standing, and in sunlight soon turns yellow. At 86° the acid commences boiling and sustains a partial decomposition; the first portions are colored yellow by the dissolved nitrogen dioxide, but subsequently, aqueous acid distils over. Nitric acid is completely decomposed into nitrogen dioxide, oxygen, and water, when its vapors are heated to about

$$2HNO_3 = 2NO_2 + H_2O + O.$$

The acid mixes in all proportions with water. Upon distilling the dilute aqueous solution, only pure water passes over at first; the boiling temperature gradually rises, and between 120° and 121° a solution goes over, which contains 68 per cent. of HNO_3, and has a specific gravity of 1.414 at 15°. This is the ordinary concentrated nitric acid of trade. When this is distilled with 5 parts of sulphuric acid, an almost anhydrous acid is obtained, which may be freed from nitrogen dioxide, contained in it, by conducting a stream of air through it.

The liquid boiling at 121°, however, can be regarded as a mixture of the trihydrate, $NO(OH)_3$, and pentahydrate, $N(OH)_5$ (pp. 193, 201).

Nitric acid is a very powerful acid, oxidizing or dissolving almost all metals (gold and platinum excepted). Nearly all the metalloids, like iodine sulphur, phosphorus, and carbon, are converted by it into their corresponding acids. It acts as a very strong oxidizing agent, destroying organic coloring substances, and decolorizes a solution of indigo very readily. In so doing the nitric acid itself is deoxidized to the lower oxidation products of nitrogen (NO and NO_2). Some substances even reduce the acid to ammonia. Thus, for example, if zinc be brought into dilute nitric acid (5–6 per cent.) the metal will be dissolved without the liberation of hydrogen. The latter, *in statu nascendi*, acts at once upon the excess of acid and reduces it to ammonia, which forms an ammonium salt with the acid; hence, in solution, we have ammonium nitrate in addition to the zinc nitrate:

$$2HNO_3 + Zn = Zn(NO_3)_2 + H_2$$

and

$$2HNO_3 + 4H_2 = NH_4NO_3 + 3H_2O.$$

If the aqueous nitric acid be less dilute (containing more than 10 per cent. of HNO_3) it will be reduced by zinc and other metals, not to ammonia, but to the nitrogen oxides, N_2O, N_2O_3, and N_2O_4. The more concentrated the acid, the higher will the oxides be.

The reduction of nitric acid to ammonia by nascent hydrogen occurs more easily in alkaline solution. If a solution of nitrates, made alkaline with sodium or potassium hydroxide, be heated with zinc or aluminium filings or iron powder, then all the nitrogen of the nitric acid will be converted into ammonia:

$$HNO_3 + 4H_2 = NH_3 + 3H_2O.$$

Hydroxylamine (p. 130) and ammonia are produced when nitric acid acts on tin.

Nitric acid usually forms salts of the form $MeNO_3$, with one equivalent of the metals; these are called nitrates, and are all readily soluble in water.

Red Fuming Nitric Acid (*Acidum nitricum fumans*) is the name given a nitric acid containing much nitrogen dioxide in solution. It is obtained by the distillation of two molecules of saltpeter with one molecule of sulphuric acid (p. 202), or better, by the distillation of commercial concentrated nitric acid with concentrated sulphuric acid. It generally has the specific gravity of 1.5–1.54, and possesses greater oxidizing power than the colorless nitric acid.

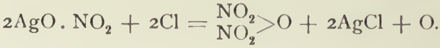
A mixture of 1 volume of nitric acid and 3 volumes of concentrated hydrochloric acid is known as *Aqua regia*, as it is able to dissolve gold and platinum, which neither of the acids alone is capable of doing. The powerful oxidizing action of the mixture is due to the presence of free chlorine and the chlorine derivative $NOCl$, which may be considered the chloranhydride of nitrous acid:

$$3HCl + HNO_3 = 2H_2O + NOCl + Cl_2.$$

Nitrogen Pentoxide, N_2O_5, nitric anhydride, is produced by carefully heating phosphoric anhydride with nitric acid:

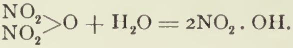
$$2HNO_3 + P_2O_5 = N_2O_5 + 2HPO_3;$$

further, together with oxygen, on conducting chlorine over silver nitrate:



$$2AgO . NO_2 + 2Cl = \begin{matrix}NO_2\\NO_2\end{matrix}\!\!>O + 2AgCl + O.$$

It forms colorless, rhombic prisms, melting at 30° and boiling with partial decomposition at 47°. It is very unstable, decomposing readily into nitrogen tetroxide and oxygen, and sometimes exploding spontaneously. It yields nitric acid with water and evolves much heat by the union:



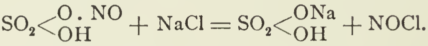
$$\begin{matrix}NO_2\\NO_2\end{matrix}\!\!>O + H_2O = 2NO_2 . OH.$$

Nitroxyl Chloride, NO_2Cl, the chloranhydride of nitric acid, results from the union of nitrogen dioxide with chlorine, and according to the ordinary method of forming chloranhydrides (see p. 195), by the action of phosphorus pentachloride or oxychloride upon nitric acid, or better, its silver salt:

$$\underset{\text{Silver nitrate.}}{3NO_2 . OAg} + POCl_3 = 3NO_2Cl + \underset{\text{Silver phosphate.}}{PO(OAg)_3}.$$

It is said to be a heavy, yellow liquid, boiling at +5°. Water immediately decomposes it into hydrochloric and nitric acids. However, Geuther's experiments make the existence of this acid rather doubtful [Ann. Chem. 245 (1888), 98].

Nitrosyl Chloride, NOCl, is produced by the union of nitric oxide (2 volumes) with chlorine (1 volume): $2NO + Cl_2 = 2NOCl$; when phosphoric chloride, PCl_5, is allowed to act upon liquid nitrogen tetroxide, N_2O_4, and by heating lead-chamber crystals (p. 208) with sodium chloride to 80–90°:

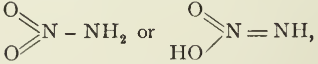


$$SO_2<\begin{matrix}O . NO\\OH\end{matrix} + NaCl = SO_2<\begin{matrix}ONa\\OH\end{matrix} + NOCl.$$

The reddish-yellow vapors that escape, if cooled to —20°, condense to a red liquid of specific gravity 1.416 at —12°, and boils at +2°. It forms nitrous and hydrochloric acids with water:

$$NOCl + H_2O = HNO_2 + HCl.$$

It may, therefore be regarded as the chloranhydride of nitrous acid—NO . OH.

Nitramide, $NO_2 . NH_2$ =  $\begin{matrix}O\\O\end{matrix}\!\!>N - NH_2$ or $\begin{matrix}O\\HO\end{matrix}\!\!>N = NH$, the amide of nitric acid, was discovered by Thiele and Lachmann on decomposing potassium nitrocarbaminate (see Organic Chemistry) with sulphuric acid. It is also produced upon adding nitric acid to a solution of potassium imidosulphonate (p. 196) in concentrated sulphuric acid:

$$NH(SO_3H)_2 + NO_2 . OH = NO_2 . NH_2 + H_2S_2O_7.$$

Nitramide crystallizes from ligroïne, in which it dissolves with difficulty, in brilliant white plates. It dissolves readily in ether, alcohol and water. It melts at about 73° with immediate decomposition into nitrous oxide and water:

$$NO_2 . NH_2 = N_2O + H_2O.$$

It volatilizes partly at the ordinary temperature. It is especially sensitive to alkalies; in contact with sodium hydroxide it explodes with fire phenomena. Its aqueous solution reacts strongly acid. It also yields a readily decomposable mercury salt:

$$NO_2NHg.$$

When nitramide is reduced hydrazine results:

$$NO_2NH_2 + 3H_2 = NH_2 . NH_2 + 2H_2O.$$

Nitramide is isomeric with hyponitrous acid: HO–N=N–OH. [See Ann. Chem. **288** (1895), 267; **296** (1897), 95.]

Nitrogen Trioxide, N_2O_3, nitrous anhydride, is formed by the direct union of nitrogic oxide (4 volumes) with oxygen (1 volume) at —18°:

$$\underset{\text{4 vols.}}{4NO} + \underset{\text{1 vol.}}{O_2} = \underset{\text{2 vols.}}{2N_2O_3};$$

by mixing liquid nitrogen tetroxide, N_2O_4, with a little cold water:

$$2\left.\begin{matrix}NO_2\\NO\end{matrix}\right\}O + H_2O = \left.\begin{matrix}NO\\NO\end{matrix}\right\}O + 2NO_2 . OH;$$

by the introduction of nitric oxide into liquid nitrogen tetroxide below —21°:

$$N_2O_4 + 2NO = 2N_2O_3;$$

and by conducting nitric oxide into cold anhydrous nitric acid:

$$2HNO_3 + 4NO = 3N_2O_3 + H_2O.$$

It is most easily obtained by the action of nitric acid upon arsenious oxide, As_2O_3. Nitrogen tetroxide is simultaneously produced, from which it is readily separated by fractional distillation and condensation.

Nitrogen trioxide condenses at —21° to a dark-blue liquid of specific gravity 1.449 at 0°, and begins to boil at 3.5°. It decomposes when distilled; its vapors consist of a mixture of the tetroxide and nitric oxide ($N_2O_4 + 2NO$) and at more elevated temperatures of nitrogen dioxide and nitric oxide ($2NO_2 + 2NO$). Upon cooling they reunite to the liquid nitrous anhydride. The latter is therefore only known in the liquid condition. Its dissociation begins at —21° [Geuther, Ann. Chem. **245** (1888), 96; see also Lunge and Porschnew, Z. f. anorg. Chem. **7** (1894), 209].

The trioxide mixed with a little cold water probably forms nitrous acid ($N_2O_3 + H_2O = 2HNO_2$); more water, aided by heat, decomposes it into nitric acid and nitric oxide gas:

$$3HNO_2 = HNO_3 + 2NO + H_2O.$$

Nitrous Acid, HNO_2, is not known in a free state. Its salts (the *nitrites*) are obtained by igniting the nitrates:

$$KNO_3 = KNO_2 + O.$$

The withdrawal of oxygen is rendered easier if oxidizable metals, *e. g.*, lead, be added to the fusion (see Potassium and Sodium Nitrite). Traces of nitrites are found in the air and in many waters.

On adding sulphuric acid to the nitrites, brown vapors are disengaged; these consist of nitrogen dioxide and nitric oxide. It may be that the nitrous acid, at first liberated, is broken down into water and the trioxide, which, as we have seen above, gradually decomposes into nitrogen dioxide, NO_2, and nitric oxide, NO. Similar reddish-brown vapors are obtained if nitric acid be permitted to act upon starch or arsenious oxide (As_2O_3).

According to Lunge, if we employ nitric acid of specific gravity 1.30–1.35, nitrogen trioxide is produced almost exclusively, whereas in using the concentrated acid (1.4–1.5) we get a mixture rich in dioxide, and if the acid be dilute the chief product is nitric oxide, NO, with a little nitrogen dioxide, NO_2.

The nitrous acid which has separated out in the solution and its decomposition products—NO_2 and NO—are strong oxidizers, setting iodine free from the soluble iodides. In other cases, however, they exhibit a reducing action; thus, *e. g.*, the acidified red solution of potassium permanganate is decolorized by the addition of nitrites, and nitrous becomes nitric acid. In very dilute aqueous solution, the action proceeds according to the following equation:

$$5HNO_2 + 2KMnO_4 + 3H_2SO_4 = 5HNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O.$$

This reaction serves for the quantitative determination of free nitrous acid, as well as for its salts (p. 208).

Nitrogen Tetroxide, N_2O_4, or *nitrogen dioxide*, NO_2 (formerly called *hyponitric acid*), only exists at low temperatures; when heated, it suffers a gradual decomposition into the simpler molecules NO_2 which recombine to N_2O_4 upon cooling. We here meet the interesting case of dissociation, occurring even at the ordinary temperature. The tetroxide, N_2O_4, is colorless, while the dioxide, NO_2, is colored red-brown; it appears, therefore, that the color gradually becomes darker as the temperature rises, and that it corresponds to the increasing dissociation of the complex molecules N_2O_4. The same was observed with sulphur tetrachloride (p. 110) and nitrogen trioxide (p. 205).

At ordinary temperatures, nitrogen tetroxide is a liquid of specific gravity 1.49. When cooled to —20° it solidifies to a colorless crystalline mass, melting at —12°. In consequence of the dissociation which begins at 0°, the liquid, at first colorless, becomes yellow, and the intensity in color grows with rising temperature. The liquid begins to boil at about 22°, and is converted into a yellowish-brown vapor which becomes dark as the temperature is increased.

The theoretical vapor density of nitrogen tetroxide, N_2O_4 equals 92.08, while that of the dioxide, NO_2, equals 46.04. The experimental vapor density has been found to equal 76 at the point at which the liquid compound boils (26°); it may be calculated from this that, at this temperature, 34.4 per cent. of the tetroxide molecules are decomposed into dioxide molecules. Hence we conclude that the dissociation of the compound N_2O_4 commences even in the liquid state ; this is confirmed by the yellow coloration appearing at 0°. With rising temperature the density of the vapor steadily diminishes, becomes constant finally at 150° and equals 46. Then all the molecules (N_2O_4) are decomposed into the simpler molecules NO_2 ; and the dark coloration of the vapors attains its maximum.

Nitrogen tetroxide is produced by conducting electric sparks through a mixture of dry nitrogen and oxygen ; it is also formed by the union of two volumes of nitric oxide with one volume of oxygen :

$$\underset{2\ \text{vols.}}{2NO} + \underset{1\ \text{vol.}}{O_2} = \underset{1\ \text{vol.}}{N_2O_4}.$$

We can get it more conveniently by heating dry lead nitrate, which decomposes according to the following equation :

$$Pb(NO_3)_2 = PbO + O + 2NO_2.$$

The escaping dioxide condenses in the cooled receiver to liquid tetroxide, N_2O_4.

Nitrogen tetroxide varies in its behavior with water, according to the temperature of the latter. We saw that by the action of a little cold water, it was decomposed into nitrogen trioxide and nitric acid (p. 205). With an excess of cold water, and also with an aqueous solution of alkalies, it yields nitric and nitrous acids, that is, their salts:

$$\begin{matrix}NO_2\\NO\end{matrix}\!\!>O + H_2O = NO_2 . OH + NO . OH.$$

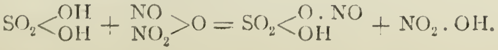
Both reactions plainly indicate that the liquid tetroxide represents the *mixed anhydride* of nitric and nitrous acids (p. 201) ; similarly, the compound Cl_2O_4 constitutes the mixed anhydride of chloric and chlorous acids (p. 117). Warm water converts the tetroxide into nitric acid and nitric oxide—because under these conditions the nitrous acid decomposes into nitric acid and nitric oxide (see p. 205). The dioxide behaves similarly :

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

The tetroxide and dioxide possess strong oxidizing properties ; many substances burn in their vapors ; iodine is set free from the soluble metallic iodides by them.

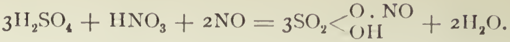
Many metals, just after the reduction of their oxides in hydrogen, absorb large quantities of nitrogen dioxide at lower temperatures, *e. g.*, copper takes up 1000 times its volume. "Nitro-metals" are produced in this way. "Nitro-copper," Cu_2NO_2, is an amorphous substance, which is decomposed by water into nitric oxide, copper, copper nitrite and nitrate [Ber. 26 (1893), IV, 361].

Nitrosylsulphuric Acid, $SO_5NH = SO_2<\begin{matrix}O . NO\\OH\end{matrix}$, termed *nitrosulphonic acid,* is an intermediate product in the manufacture of commercial sulphuric acid (see p. 190), and is quite important for the determination of the nitrogen oxides. It is produced by conducting nitrogen tetroxide into concentrated sulphuric acid :



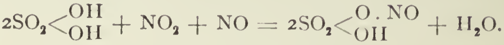
$$SO_2<\begin{matrix}OH\\OH\end{matrix} + \begin{matrix}NO\\NO_2\end{matrix}\!\!>O = SO_2<\begin{matrix}O . NO\\OH\end{matrix} + NO_2 . OH.$$

Nitrogen monoxide, NO, is not absorbed by pure sulphuric acid, but will be if the same contains nitric acid:



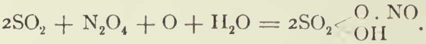
$$3\mathrm{H_2SO_4} + \mathrm{HNO_3} + 2\mathrm{NO} = 3\mathrm{SO_2}<^{\mathrm{O.NO}}_{\mathrm{OH}} + 2\mathrm{H_2O}.$$

Therefore it results upon conducting nitrous acid vapors into concentrated sulphuric acid:



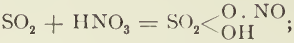
$$2\mathrm{SO_2}<^{\mathrm{OH}}_{\mathrm{OH}} + \mathrm{NO_2} + \mathrm{NO} = 2\mathrm{SO_2}<^{\mathrm{O.NO}}_{\mathrm{OH}} + \mathrm{H_2O}.$$

Further, the nitrosylsulphuric acid results from the combined action of sulphur dioxide, nitrogen tetroxide, oxygen, and a little water:



$$2\mathrm{SO_2} + \mathrm{N_2O_4} + \mathrm{O} + \mathrm{H_2O} = 2\mathrm{SO_2}<^{\mathrm{O.NO}}_{\mathrm{OH}}.$$

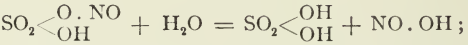
It is obtained most readily by conducting sulphur dioxide into strongly cooled anhydrous nitric acid:



$$\mathrm{SO_2} + \mathrm{HNO_3} = \mathrm{SO_2}<^{\mathrm{O.NO}}_{\mathrm{OH}};$$

there results a thick magma, which may be dried upon porous earthen plates under the desiccator.

Nitrosylsulphuric acid forms a leafy or granular crystalline, white mass (lead-chamber crystals, p. 191), which melts at about 73° and decomposes into its anhydride, sulphuric acid, and nitrogen oxides. It deliquesces in moist air, and yields sulphuric and nitrous acids with water:

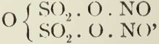


$$\mathrm{SO_2}<^{\mathrm{O.NO}}_{\mathrm{OH}} + \mathrm{H_2O} = \mathrm{SO_2}<^{\mathrm{OH}}_{\mathrm{OH}} + \mathrm{NO.OH};$$

the nitrous acid decomposes further into nitric acid and nitric oxide (p. 205).

Nitrosylsulphuric acid dissolves in concentrated sulphuric acid without any change; the solution, called *nitroso-acid*, is also produced in the sulphuric acid manufacture in the Gay-Lussac tower (p. 190), is very stable and may be distilled without decomposition. When diluted with water it remains unaltered at first, but when the specific gravity of the solution reaches 1.55–1.50 (51–48° Bé.), then all the nitrogen oxides escape, especially on warming. When the nitroso-acid is poured into a large quantity of water, the nitrososulphuric acid breaks down into sulphuric and nitrous acids, and the latter in part into nitric acid and nitric oxide.

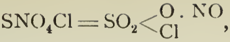
All the nitrogen oxides and acids are separated as nitric oxide (NO) on shaking the nitroso-acid with mercury—a procedure serving equally well for estimating the amount of nitroso-acid by means of the nitrometer. Sulphur dioxide acts similarly and upon this depends the denitrating action of the *Glover tower* (see pp. 189, 190).



The *anhydride* of nitrosylsulphuric acid, $\mathrm{S_2N_2O_9} = \mathrm{O}\left\{\begin{matrix}\mathrm{SO_2.O.NO}\\ \mathrm{SO_2.O.NO}\end{matrix}\right.$, is produced upon heating the acid (together with sulphuric acid, nitric oxide, and nitrogen dioxide) beyond its point of fusion. It is obtained pure by saturating sulphur trioxide with nitric oxide:

$$3\mathrm{SO_3} + 2\mathrm{NO} = \mathrm{O(SO_2.O.NO)_2} + \mathrm{SO_2}.$$

It is a crystalline, colorless mass, melting at 217°, and boiling without decomposition at about 360°. Much water decomposes it, the same as nitrosylsulphuric acid.

The *chloranhydride* of nitrosylsulphuric acid,  $SNO_4Cl = SO_2<\begin{matrix}O\,.\,NO\\Cl\end{matrix}$, is formed by the union of sulphur trioxide with nitrosyl chloride:

$$SO_3 + NOCl = SO_2Cl(O\,.\,NO).$$

It forms white leaflets, is decomposed by heat into its components, and with water breaks down into sulphuric, hydrochloric, and nitrous acids.

Nitric Oxide, NO. When different metals are dissolved in somewhat dilute nitric acid this oxide is formed. It is conveniently obtained by pouring dilute nitric acid (specific gravity 1.2) upon copper filings:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

A better procedure consists in pouring a saturated solution of saltpeter upon thin copper turnings and then gradually introducing concentrated sulphuric acid, or a concentrated sodium nitrite solution is allowed to flow gradually into a hydrochloric acid solution of ferrous chloride or sulphate:

$$FeCl_2 + NaNO_2 + 2HCl = FeCl_3 + NaCl + H_2O + NO.$$

The evolution begins in the cold [see Thiele, Ann. Chem. (1889) **253**, 246].

A constant stream of very pure nitric oxide may be obtained by pouring concentrated sulphuric acid, containing about 2 per cent. of sodium nitrite [Emich, Monatsh. f. Chem. (1892), XIII, 73], upon mercury. Also by mixing a nitrite solution with one of potassium ferrocyanide and acetic acid [Deventer, Ber. **26** (1893), I, 589].

A colorless gas escapes, which, however, immediately forms brown vapors when it comes in contact with the air, as it unites with the oxygen of the latter to form nitrogen dioxide. Therefore, all the air must be expelled from the generating vessel by nitric oxide, and the gas collected over water after the interior of the apparatus has become colorless.

Nitric oxide is a colorless gas. Under normal conditions one liter of it weighs 1.3426 grams; its gas density also remains unchanged at —100° (in comparison with air of the same temperature, V. Meyer). It is condensed with difficulty. Its critical temperature is —93°, and its critical pressure 71 atmospheres (p. 48). Liquid nitric oxide is colorless. It boils at —153.6° and solidifies at —167° to a white mass. It is slightly soluble in water, but dissolves very readily in an aqueous solution of ferrous salts, imparting a dark-brown color to the liquid; heat expels it from the same.

Nitric oxide is readily soluble in nitric acid. As its solution becomes more concentrated, it assumes a brown, yellow, green or blue color, as nitrogen trioxide is formed finally with anhydrous nitric acid:

$$2HNO_3 + 4NO = 3N_2O_3 + H_2O.$$

Potassium permanganate oxidizes it, like nitrous acid (p. 206), to nitric acid:

$$10NO + 6KMnO_4 + 9H_2SO_4 = 10HNO_3 + 3K_2SO_4 + 6MnSO_4 + 4H_2O.$$

As nitric acid contains 53.3 per cent. of oxygen, it is capable of sustaining the combustion of some substances, but only those in whose combustion enough heat is liberated to effect the breaking down of nitric oxide into nitrogen and oxygen. Hence, phosphorus continues to burn in this gas, while a sulphur flame, developing only a slight heat, is extinguished; ignited charcoal does the same, while a splinter, burning energetically, will continue to do so, when introduced into the gas. On shaking a cylinder filled with nitric oxide with a few drops of readily volatile carbon bisulphide, and bringing a flame to the mouth of the vessel, the carbon bisulphide vapors will quietly burn in the gas, giving a bright, luminous flame, emitting strong actinic rays; in this combustion, the carbon and sulphur of the carbon bisulphide unite with the oxygen of the nitric oxide and form carbon dioxide and sulphur dioxide.

Nitric oxide is a strongly endothermic compound (see p. 212), and is consequently explosive (p. 30).

On determining the quantity of heat disengaged in the combustion of phosphorus, carbon or other substances in this gas, it will be discovered that the same is greater (about 21.5 Cal.) than that which is developed by the combustion of these bodies in oxygen. This can only be explained upon the theory that less heat is necessary for the separation of NO into N and O than for the separation of the molecules of combined oxygen atoms —an additional proof that the molecules of free oxygen (as of other elements) consist of atoms.

With oxygen or air, nitric oxide at once forms brown vapors of nitrogen dioxide:

$$\underset{\text{2 vols.}}{2NO} + \underset{\text{1 vol.}}{O_2} = \underset{\text{2 vols.}}{2NO_2}.$$

With less oxygen, nitrogen trioxide is produced (p. 205). Nitric oxide also combines with chlorine to nitrosyl chloride, NOCl (p. 204), and with bromine it yields nitrosyl bromide, NOBr. At a red heat nitric oxide becomes nitrogen dioxide and nitrogen. With hydrogen and moderate heat it forms water and nitrogen:

$$NO + H_2 = N + H_2O;$$

a mixture of both gases burns with a greenish-white flame. On conducting a mixture of nitric oxide and hydrogen over platinum sponge, water and ammonia are produced:

$$2NO + 5H_2 = 2NH_3 + 2H_2O.$$

The volumetric analysis of nitric oxide gas may be easily executed as follows: Fill a bent glass tube over mercury with the gas; introduce into the same a piece of sodium and heat the latter with a lamp. The sodium combines with the oxygen, and free nitrogen separates; the volume of the latter always equals half the volume of the nitric oxide gas employed; this follows from the formula NO:

$$\underset{\text{2 vols.}}{2NO} = \underset{\text{1 vol.}}{N_2} + \underset{\text{1 vol.}}{O_2}.$$

In nitrogen dioxide nitrogen appears to be quadrivalent, in nitric oxide bivalent, while usually it is trivalent or quinquivalent. Attention has already been called to the similarity of nitrogen dioxide and chlorine dioxide, ClO_2 (p. 207).

Nitrous Oxide, N_2O, is formed when zinc or tin acts upon dilute nitric acid of specific gravity 1.1. It may be best obtained by heating ammonium nitrate, which at about 170° breaks down directly into water and nitrous oxide:

$$NH_4NO_3 = N_2O + 2H_2O.$$

It is very probable that nitramide, $NO_2 . NH_2$, is produced transitionally, but it immediately decomposes into water and nitrous oxide (p. 204). The decomposition is very energetic at about 240° and is frequently accompanied with explosion. It is advisable to use a well-dried mixture of equivalent quantities of sodium nitrate and ammonium sulphate. The reaction will then proceed quietly, beginning at 230°, and no explosion will occur (Smith).

The formation of the oxide from hydroxylamine nitrite (the isomeride of ammonium nitrate) is interesting. The decomposition takes place in aqueous solution and proceeds according to the equation:

$$NO_2 . NH_3OH = N_2O + 2H_2O.$$

Nitrous oxide is a colorless gas, of sweetish taste and slight odor. Its density corresponds to the molecular formula $N_2O = 44.08$. One liter weighs under normal conditions 1.9706 grams. In cold water it is tolerably soluble (1 volume of water dissolves at 0° 1.305 volumes of nitrous oxide); therefore it must be collected over warm water or mercury. By pressure and cold it condenses to a colorless liquid of specific gravity 0.937 and boils under the ordinary pressure at —89.8°. By rapid evaporation, liquid nitrous oxide solidifies to a crystalline mass which remelts at —102.3°. If the aqueous nitrous oxide be evaporated over an air-pump its temperature falls to —140°. Its critical temperature is +38.8°; critical pressure, 775 atmospheres (p. 48).

Although this oxide contains less oxygen than nitric oxide, it supports the combustion of many bodies more readily than the latter, because it is more easily decomposed into oxygen and nitrogen. A glimmering chip inflames in it, as in oxygen; phosphorus burns in it with a bright, luminous flame, while a sulphur flame liberating very little heat is extinguished. A mixture of equal volumes of nitrous oxide and hydrogen explodes like detonating gas, only less violently:

$$\underset{\text{1 vol.}}{N_2O} + \underset{\text{1 vol.}}{H_2} = \underset{\text{1 vol.}}{N_2} + \underset{\text{1 vol.}}{H_2O}.$$

It resembles oxygen very much, but can be distinguished from it by not producing brown vapors with nitric oxide, as does the former. It is not capable of combining with oxygen. When it is conducted through a red-hot tube it is decomposed into nitrogen and oxygen. It has an exhilarating effect when inhaled in slight quantity, and is, therefore, termed *laughing gas*.

Its volume composition may be determined in the same manner as with nitric oxide, viz., by heating a definite volume of the gas with potassium. Then we learn that from one volume of nitrous oxide an equal volume of nitrogen will be separated—corresponding to the molecular formula:

$$\underset{\text{1 vol.}}{N_2O} + K_2 = \underset{\text{1 vol.}}{N_2} + K_2O.$$

Hyponitrous Acid, $H_2N_2O_2 = HO{-}N{=}N{-}OH$. In the list of reduction products of nitric acid extending as far down as ammonia:

$$HNO_3, \quad HNO_2, \quad (HNO)_2, \quad NH_2OH, \quad NH_3,$$

this acid occupies a position between nitrous acid and hydroxylamine. Accordingly, it can be obtained—

(1) by the reduction of nitric and nitrous acids;
(2) by the oxidation of hydroxylamine; and
(3) by the union of nitrous acid and hydroxylamine with the exit of water.

The reduction of the salts of nitric or nitrous acids may be effected by sodium amalgam or by electrolysis; the oxidation of hydroxylamine in aqueous solution by various metallic oxides, but especially by mercuric oxide: $2NH_2OH + 2HgO = HON{=}NOH + 2H_2O + 2Hg$. To obtain hyponitrous acid according to (3) allow sodium nitrite and hydroxylamine sulphate to interact, when sodium sulphate and hydroxylamine nitrite will result: $2NaNO_2 + SO_4(NH_4O)_2 = Na_2SO_4 + 2NO_2 . NH_4O$, which for the most part breaks down into water and nitrous oxide (p. 212), but in small amount to water and hyponitrous acid: $HONH_2 + ON . OH = HON{=}NOH + H_2O$. Divers claims that good yields of potassium hyponitrite can be obtained by boiling potassium hydroxylamine sulphonate (p. 197) with caustic potash: $2NH(OH)SO_3K + 4KOH = K_2N_2O_2 + 2K_2SO_3 + 4H_2O$. Upon neutralizing the hyponitrite solution, obtained by one or the other method, with acetic acid and adding silver nitrate the silver salt $Ag_2N_2O_2$ separates as a bright yellow, amorphous powder, which slowly decomposes at 100°, but at 110° with violent explosion. Concentrated sulphuric acid liberates nitrous oxide from it.

The acid may be obtained in ethereal solution by adding gradually an excess of its silver salt to a solution of dry hydrogen chloride in anhydrous ether. After evaporating the ethereal solution in a vacuum, free hyponitrous acid remains in crystalline leaflets. It explodes readily—with flame—on coming in contact with solid caustic potash; deliquesces in the air, is very soluble in alcohol, and soluble in benzene and in chloroform. It is more stable in aqueous solution than in the solid condition, but even then readily decomposes into nitrous oxide and water: $H_2N_2O_2 = N_2O + H_2O$. It therefore bears the same relation to nitrous oxide as nitric acid to nitrogen pentoxide, and nitrous acid to nitrogen trioxide; however, nitrous oxide does not take up water and it, therefore, does not behave like the true anhydride of hyponitrous acid. Upon neutralizing its aqueous solution with caustic soda the acid salt $NaHN_2O_2$ is produced, which quickly breaks down into caustic soda and nitrous oxide: $NaHN_2O_2 = N_2O + NaOH$. The freshly prepared solution of the acid liberates iodine from potassium iodide after it has stood for some time; this is because it decomposes very slowly and only to a slight degree into nitrous acid and ammonia: $3H_2N_2O_2 = 2N_2O_3 + 2NH_3$. It decolorizes potassium permanganate and becomes nitric acid.

The molecular magnitude of the acid was established by the determination of the vapor density of its ethyl ester, $N_2O_2(C_2H_5)_2$, by Zorn, and from the molecular weight of the benzyl ester, $N_2O_2(C_7H_7)_2$, by Hantszch and Kaufmann.

Hyponitrous acid is isomeric with nitramide (p. 204).

Compare the investigations of Hantzsch and his co-workers: Ann. Chem. **292** (1896), 317; **299** (1898), 94; Divers *ibid.* **295** (1897), 366; also Kirschner, Z. f. anorg. Chem. **16** (1898), 424.

The *thermo-chemical* relations of the oxygen derivatives of nitrogen give some clue to their chemical deportment. All nitrogen oxides are endothermic compounds, *i. e.*, they are produced from their elements with heat absorption corresponding to the symbols:

$$(N_2, O) = -17.5 \quad (N, O) = -21.6 \quad (N, O_2) = -8.$$

From this we observe that the oxides of nitrogen cannot be prepared from the elements without addition of energy. Proceeding from nitric oxide (NO), we see from the above numbers that the formation of the higher oxides from it occurs with heat disengagement:

$$(2NO, O) = 20.1 \quad (NO, O) = 13.4 \quad (2NO_2, O_2) = 40.5,$$

whereas heat is absorbed in the conversion of nitrous into nitric oxide: $(N_2O, O) = -25.4$. (See J. Thomsen's Thermochemische Untersuchungen, IV, 314.)

Heat disengagement, on the contrary, occurs in the production of nitric acid from its elements:

$$(N,O_3,H\text{–liquid}) = 41.6 \quad (N,O_3,H,Aq) = 49.1.$$

This explains the relative stability of that acid.

Compounds of Nitrogen with Sulphur.—Two such bodies are known: *nitrogen sulphide*, N_4S_4, corresponding in composition to a quadrupled nitric oxide, and *nitrogen pentasulphide*, corresponding to nitric anhydride, N_2O_5.

Nitrogen sulphide, N_4S_4, is produced when dry ammonia, in benzene solution, acts upon sulphur dichloride:

$$4NH_3 + 6SCl_2 = N_4S_4 + 12HCl + S_2.$$

It consists of orange-red needles, melting at 178°. It detonates at higher temperatures or when struck. Its molecular weight has been determined by methods which will be described under Solutions.

Nitrogen pentasulphide, N_4S_5, is formed by a complicated reaction occurring on heating nitrogen sulphide with carbon bisulphide to 100° in a sealed tube. It is a deep-red liquid, transparent in thin layers with a blood-red color. It is very mobile, not moistening glass and its specific gravity at 18° equals 1.90. It solidifies by cold to a mass resembling iodine and melts at 10°. Its odor is like that of iodine and is at the same time sweet. Nitrogen pentasulphide is not soluble in water, but in organic solvents. Its solutions are more stable than the pure pentasulphide, which easily decomposes into its elements. Boiling water, alkalies and hydrogen sulphide decompose the pentasulphide very readily with the production of ammonia and the separation of sulphur. [See Z. f. anorg. Chem. 13 (1897), 200.]

2. OXYGEN COMPOUNDS OF PHOSPHORUS.

. .	H_3PO_2 Hypophosphorous acid.
P_4O_6 Phosphorus trioxide.	H_3PO_3 Phosphorous acid.
P_2O_5 Phosphorus pentoxide.	H_3PO_4. Orthophosphoric acid.

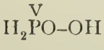
Oxides containing less oxygen, *e. g.*, the tetroxide P_2O_4 and the oxide P_2O, are not definitely known.

The following anhydride acids are derived from orthophosphoric acid:

HPO_3, Metaphosphoric acid.
$H_4P_2O_7$, Pyrophosphoric acid.

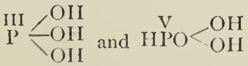
Orthophosphoric acid also yields an anhydride acid with phosphorous acid: hypophosphoric acid, $H_4P_2O_6$.

The structure of these compounds is expressed by the following formulas:



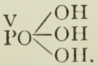
$$H_2\overset{V}{P}O{-}OH$$

Hypophosphorous acid.



$$\overset{III}{P}\!\left\langle\begin{array}{l}OH\\OH\\OH\end{array}\right. \text{ and } H\overset{V}{P}O\!\left\langle\begin{array}{l}OH\\OH\end{array}\right.$$

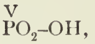
Phosphorous acid.



$$\overset{V}{P}O\!\left\langle\begin{array}{l}OH\\OH\\OH.\end{array}\right.$$

Phosphoric acid.

In hypophosphorous acid two atoms of hydrogen are in direct union with quinquivalent phosphorus, while the third hydrogen atom forms an hydroxyl group with oxygen. It is only this last atom of hydrogen which is readily replaced by the action of bases; hence hypophosphorous acid is a *monobasic acid.* Phosphorous acid (like sulphurous and arsenious acids) appears in two forms in its derivatives (pp. 186, 221). It is very probable that in its salts it has one atom of hydrogen and two hydroxyl groups joined to phosphorus; consequently it is a *dibasic acid.* [See Michaelis and Becker, Ber. **30** (1897), 1003.] Finally, three series of salts and three hydroxyls are assumed to be present in phosphoric acid. By the elimination of one molecule of water from phosphoric acid, metaphosphoric acid results—an anhydride which, at the same time, is a monobasic acid, as it contains one hydroxyl group:



$$\overset{V}{P}O_2\text{–}OH$$

, Metaphosphoric acid.

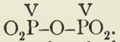
On removing one molecule of water from two molecules of phosphoric acid, pyro- or diphosphoric acid is formed (see p. 193):

2 molecules Phosphoric acid.

1 molecule Pyrophosphoric acid.

Pyrophosphoric acid contains four hydroxyl groups, hence is tetrabasic. Similarly, hypophosphoric acid results from one molecule each of phosphoric acid and phosphorous acid, $P(OH)_3$.

Finally, if from two molecules of phosphoric acid all the hydrogen atoms be removed, in the form of water, an anhydride remains:



$$O_2\overset{V}{P}\text{–}O\text{–}\overset{V}{P}O_2.$$

Phosphoric anhydride.

The salts of phosphoric acid are termed *phosphates;* those of phosphorous acid, *phosphites*, and of hypophosphorous acid, *hypophosphites.*

Hypophosphorous Acid, H_3PO_2. Hydrogen phosphide escapes when a concentrated solution of sodium or barium hydroxide is warmed with yellow phosphorus, leaving behind in solution a salt of hypophosphorous acid:

$$4P + 3NaOH + 3H_2O = 3H_2PO.ONa + PH_3$$
$$8P + 3Ba(OH)_2 + 3H_2O = 3(H_2PO.O)_2Ba + 2PH_3.$$

The free acid may be separated from the barium salt by means of sulphuric acid; the insoluble barium sulphate being filtered off from the aqueous solution of the acid, and the latter concentrated under the air-pump. Hypophosphorous acid is a colorless, thick liquid, with a strong acid reaction. Below 0° it sometimes solidifies to large, white leaflets, which melt at +17.4°. Heat converts it, with much foaming, into hydrogen phosphide and phosphoric acid:

$$2H_3PO_2 = PH_3 + H_3PO_4.$$

It absorbs oxygen readily, becoming phosphoric acid, hence acts as a powerful reducing agent. It reduces sulphuric acid to sulphur dioxide, and even to sulphur. It precipitates many of the metals from their solutions; from copper sulphate it separates the hydride Cu_2H_2.

The acid is monobasic, $H_2PO.OH$ (see p. 214). Its salts dissolve readily in water, and absorb oxygen from the air, thus becoming phosphates. When heated in a dry condition, they set free phosphine and hydrogen and are converted into pyro- and metaphosphates; some also yield metallic phosphides. Nascent hydrogen reduces hypophosphorous acid to phosphine.

Phosphorous Acid, H_3PO_3, is formed at the same time with phosphoric acid and hypophosphoric acid in the slow oxidation of phosphorus in moist air. The decomposition of phosphorus trichloride by water gives it more conveniently:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

By evaporating this solution under the air-pump the phosphorous acid becomes crystalline. The crystals are readily soluble in water, and deliquesce in the air. It melts at 70°, and decomposes on further heating into phosphine and phosphoric acid:

$$4H_3PO_3 = PH_3 + 3H_3PO_4.$$

In the air the acid absorbs oxygen, and changes to phosphoric acid. Hence, it is a strong reducing agent, and precipitates the free metals from many of their solutions. In the presence of water the halogens oxidize it to phosphoric acid.

It is a dibasic acid, forming two series of salts, in which one or two atoms[*] of hydrogen are replaced by metals. The phosphites do not oxidize in the air, except under the influence of strong oxidizing agents When heated, they generally decompose into hydrogen, pyrophosphates and phosphide. Nascent hydrogen also reduces phosphorous acid to phosphine—a circumstance of importance in the detection of phosphorus-poisoning.

Phosphorous Anhydride, or phosphorus trioxide according to the old formula P_2O_3, has been shown by Thorpe and Tutten (1892) to be correctly expressed by P_4O_6. It is

---

[*] Therefore, the structural formula, $HPO(OH)_2$ is assigned to this acid. There appears to exist another phosphorous acid, at least in compounds, to which the formula $P(OH)_3$ belongs (pp. 213, 216).

produced on conducting dry air over gently heated phosphorus, or by carefully heating phosphorous acid with phosphorus trichloride:

$$2H_3PO_3 + 2PCl_3 = P_4O_6 + 6HCl.$$

It is a white, flocculent mass or it consists of colorless needles. It melts at 22.5°, sublimes readily and boils in an atmosphere of nitrogen at 173°. Its vapor density corresponds to the formula P_4O_6. At 400° it breaks down into phosphorus and phosphorus tetroxide, P_2O_4, which crystallizes. It is decomposed by water in a very complicated manner.

Phosphoric Acid, H_3PO_4, or *Orthophosphoric acid*, is produced when the pentoxide is dissolved in hot water, and by the decomposition of phosphorus pentachloride or phosphorus oxychloride ($POCl_3$) by water (see p. 219). It may be obtained by decomposing bone ash, $Ca_3(PO_4)_2$, with sulphuric acid, or better, by oxidizing yellow phosphorus with nitric acid. The aqueous solution is evaporated to dryness in a platinum dish. The anhydrous acid consists of colorless, hard, prismatic crystals, which in the air deliquesce to a thick, acid liquid.

Phosphoric acid is tribasic, forming three series of salts, called *primary* (KH_2PO_4), *secondary* (K_2HPO_4), and *tertiary* (K_3PO_4). They may be spoken of according to the number of hydrogen atoms replaced by metals, as, *e. g.*, monopotassium phosphate (KH_2PO_4), dipotassium phosphate (K_2HPO_4), and tripotassium phosphate (K_3PO_4). The salts of the first two series contain hydrogen, replaceable by metals, hence may be termed acid, while the salts of the third series are neutral. Their behavior with litmus does not harmonize with this view (see Sodium Phosphate).

The tertiary phosphates, excepting the salts of the alkalies, are insoluble in water. With a silver nitrate ($AgNO_3$) solution, soluble phosphates give a *yellow* precipitate of silver phosphate, Ag_3PO_4.

Pyrophosphoric Acid, $H_4P_2O_7$ (structure, p. 214), is formed by the continuous heating of orthophosphoric acid to 260°, until a portion of it dissolved in ammonium hydroxide does not yield a yellow but a pure white precipitate with silver nitrate. The sodium salt is easily obtained by heating disodium phosphate:

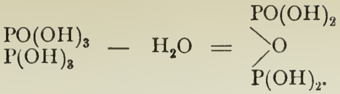
$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

Other salts are similarly formed by heating the corresponding orthophosphates.

The acid presents a white crystalline appearance, and is readily soluble in water. When in solution, it slowly takes up water at ordinary temperatures, more rapidly when heated, and, like all true anhydrides, passes into the corresponding acid—orthophosphoric acid.

Pyrophosphoric acid is tetrabasic. Its salts are very stable, and are not altered by boiling with water; warmed with dilute acids, they become salts of the ortho-acid. The soluble salts yield a *white* precipitate of silver pyrophosphate, $Ag_4P_2O_7$, with silver nitrate.

Hypophosphoric Acid, $H_4P_2O_6$. While pyrophosphoric acid is an anhydride acid of phosphoric acid, the so-called hypophosphoric may be viewed as a mixed anhydride of phosphoric and symmetrical phosphorous acids.



$$\begin{matrix}PO(OH)_3\\ P(OH)_3\end{matrix} - H_2O = \begin{matrix}PO(OH)_2\\ \rangle O\\ P(OH)_2.\end{matrix}$$

It is produced, as demonstrated by Salzer in 1877, together with phosphorous and phosphoric acids, by the slow oxidation of moist phosphorus in the air. It is separated from these acids by means of its difficultly soluble sodium salt, $Na_2H_2P_2O_6 + 6H_2O$; by precipitating the solution of the latter with a soluble lead salt we get insoluble lead hypophosphate, $Pb_2P_2O_6$. Its silver salt is more easily obtained by oxidizing phosphorus in the presence of silver nitrate. The free acid separated from the lead or silver salt by hydrogen sulphide is rather stable in a dilute solution, and below 30° may be concentrated to a syrup. At higher temperatures, more readily in the presence of hydrochloric or sulphuric acid, the acid decomposes into phosphoric and phosphorous acids. It does not reduce metallic salts, but is oxidized by potassium permanganate to phosphoric acid. [Salzer, Ann. Chem. 211 (1892), 1. See Z. f. anorg. Chem. 6 (1894), 132, for a convenient method for its production.]

Metaphosphoric Acid, HPO_3 or $PO_2 . OH$, results upon heating the ortho- or pyro-acid to 300°. It can be more conveniently obtained by dissolving phosphorus pentoxide in cold water:

$$P_2O_5 + H_2O = 2HPO_3.$$

It is a vitreous, transparent mass (*Acidum phosphoricum glaciale*), which generally contains less hydrogen than is required by the formula HPO_3. This probably is because some anhydride is present in it. It melts when heated and volatilizes at higher temperatures, without suffering any change. It deliquesces in the air, and dissolves with ease in water. (Commercial glacial phosphoric acid contains sodium and magnesium phosphate, and dissolves with difficulty in water.) The solution coagulates albumin; this is a characteristic method of distinguishing meta- from ortho- and pyrophosphoric acid. In aqueous solution, metaphosphoric acid changes, gradually at ordinary temperature, rapidly by boiling, into orthophosphoric acid:

$$HPO_3 + H_2O = H_3PO_4.$$

It is a monobasic acid. Its salts, the metaphosphates, are readily obtained by the ignition of the primary salts of the ortho-acid:

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

When the aqueous solutions of these salts are boiled, they are converted into the primary salts of orthophosphoric acid. With silver nitrate the soluble *metaphosphates* give a *white* precipitate of silver metaphosphate, $AgPO_3$.

In addition to the ordinary salts of metaphosphoric acid, various modifications of the same exist; these are derived from the polymeric meta-acids, $H_2P_2O_6$, $H_3P_3O_9$, $H_4P_4O_{12}$, etc. They are all changed to primary ortho-phosphates by boiling their solutions. [See Tammann, Jr. prakt. Ch. 45 (1892), 417.]

Phosphorus Pentoxide, P_2O_5, or *Phosphoric anhydride,* is obtained by burning phosphorus in a current of dry oxygen or dry air.

The following procedure serves for the preparation of it (Fig. 65): A piece of phosphorus, placed in an iron dish attached to the glass tube *a b*, is burned in the glass balloon *A*. The necessary amount of air is drawn through the vessel by means of an aspirator. The air is first passed through the bent tube containing pieces of pumice-stone, moistened with sulphuric acid, in order to dry it perfectly. After the phosphorus has been consumed, fresh pieces of it are introduced into the little dish through *a b*, and the upper end of the tube closed with a cork. The phosphorus pentoxide formed collects partly in *A* and partly in the receiver (*h*).

Phosphorus pentoxide is a white, voluminous, flocculent mass. It attracts moisture energetically and deliquesces in the air. It dissolves in cold water with hissing and yields metaphosphoric acid. Owing to its great affinity for water it serves as an agent for drying gases, and also for the withdrawal of water in chemical reactions, *e. g.*, in the formation of acid anhydrides from acids (p. 204).

It generally contains oxides of lower oxygen content. It can be freed from these by subliming it over ignited platinum sponge in a current of oxygen.

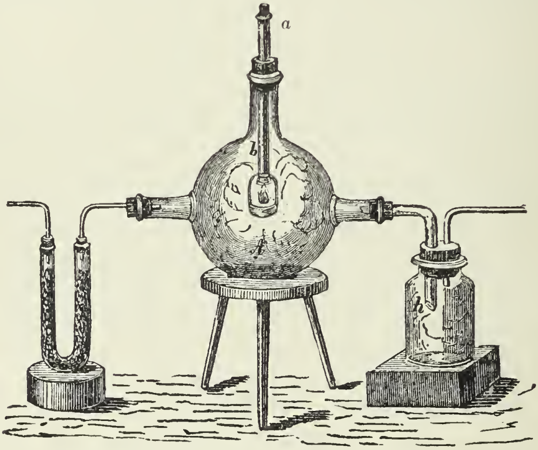


FIG. 65.

Chloranhydrides of the Acids of Phosphorus.—The halogen derivatives of phosphorus, considered on p. 141, may be viewed as the halogen anhydrides of phosphorous and phosphoric acids (p. 195). The compounds PCl_3, PBr_3, and PI_3 are derived from phosphorous acid, because they yield the latter acid with water:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

The compounds, phosphorus pentachloride, PCl_5, and phosphorus pentabromide, PBr_5, correspond to the normal orthophosphoric acid, $P(OH)_5$, which has not been obtained in a free condition (see Calcium Phosphate).

Phosphorus Oxychloride, $POCl_3$, can be viewed as the chloride of the known orthophosphoric acid, $PO(OH)_3$. It is a colorless liquid, fuming strongly in the air; its specific gravity equals 1.68 at 15°. It congeals on cooling and then melts at —1.5°. It boils without decomposition at 107°; its vapor density corresponds to the formula—

$$POCl_3 = 153.0.$$

Water decomposes it into meta- or orthophosphoric acid and hydrochloric acid:

$$POCl_3 + 2H_2O = HPO_3 + 3HCl$$
$$POCl_3 + 3HO_2 = H_3PO_4 + 3HCl.$$

It may be obtained by decomposing the pentachloride with a little water (see above), or by allowing it to deliquesce gradually in moist air. A more practical method consists in distilling the pentachloride with phosphorus pentoxide:

$$3PCl_5 + P_2O_5 = 5POCl_3;$$

or with crystallized boric acid (6 parts to 1 part):

$$3PCl_5 + 2H_3BO_3 = 3POCl_3 + B_2O_3 + 6HCl.$$

A noteworthy formation of the oxychloride is the union of phosphorus trichloride with oxygen on passing ozonized air through it:

$$PCl_3 + O_3 = POCl_3 + O_2.$$

Potassium chlorate acts in a corresponding manner very energetically upon the trichloride with the production of oxychloride:

$$3PCl_3 + KClO_3 = 3POCl_3 + KCl.$$

The compound $PSCl_3$ is analogous to the oxychloride $POCl_3$. It is obtained by heating the trichloride and sulphur to 130°; also by the action of phosphorus pentachloride upon hydrogen sulphide or some metallic sulphides:

$$PCl_5 + H_2S = PSCl_3 + 2HCl.$$

Phosphorus sulphochloride, $PSCl_3$, is a colorless liquid of specific gravity 1.6, fuming in the air and boiling at 124–125°. Water decomposes it into phosphoric and hydrochloric acids and hydrogen sulphide:

$$PSCl_3 + 4H_2O = H_3PO_4 + 3HCl + H_2S.$$

The chlorides PO_2Cl and $P_2O_3Cl_4$, corresponding to meta- and pyrophosphoric acids, have also been prepared. (See Chem. Centralblatt, 1897, II, 14.)

COMPOUNDS OF PHOSPHORUS WITH SULPHUR.

With sulphur, phosphorus affords a number of compounds which are obtained by direct fusion of phosphorus with sulphur. As the union of ordinary phosphorus and sulphur usually occurs with violent explosion, red phosphorus should be employed in preparing these compounds.

The compounds P_2S_3 and P_2S_5, analogous in constitution to P_4O_6 and P_2O_5, are solid crystalline substances, melting at higher temperatures and subliming without decomposition; phosphorus pentasulphide boils at 520° and the trisulphide at 540° (cor.). Water changes them to hydrogen sulphide and the corresponding acids, phosphorous and phosphoric. They combine with the alkaline sulphides to form compounds (*e. g.*, K_3PS_4) which possess a constitution analogous to that of the salts of phosphoric and phosphorous acids [see Sulpho-salts of Arsenic, p. 223; also Glatzel, Z. f. anorg. Chem. 4 (1893), 187].

Well-crystallized sulphur phosphides, the composition of which corresponds to the formulas P_4S_7, P_4S_3 and P_3S_6, have been prepared. The supposed compounds P_2S and P_4S are liquids which inflame readily in contact with air, but have been proved to be mixtures containing free phosphorus.

Besides the preceding, we have other phosphorus derivatives which contain nitrogen. These have been little studied, and at present are unimportant. Such compounds are PN_2H (phospham), PNO, $PNCl_2$. The so-called amid-derivatives, $POCl_2.NH_2$, $POCl(NH_2)_2$ and $PO(NH_2)_3$, are produced by allowing ammonia to act upon phosphorus oxychloride, $POCl_3$. In these chlorine is replaced by the amido-group NH_2.

Recently, amidophosphoric acid, $PO(NH_2)(OH)_2$, corresponding to sulphamic acid, $SO_2(NH_2)OH$, and imidophosphoric acid, $NH<\begin{matrix}PO(OH)_2\\PO(OH)_2\end{matrix}$, the counterpart of imidosulphuric acid, as well as its derivatives, have been more exhaustively studied [Stokes, Jahrb. d. Chem. VI (1896), 89].

---

3. OXYGEN DERIVATIVES OF ARSENIC.

As_2O_3 Arsenic trioxide.	. . . .
As_2O_5 Arenic pentoxide.	H_3AsO_4. Arsenic acid.

Arsenic Trioxide, As_2O_3, or *Arsenious anhydride* (*Acidum arseniosum*), occurs in nature as arsenic "bloom." It is produced by the burning of arsenic in oxygen or in the air, and by the oxidation of the metal with dilute nitric acid. It is obtained metallurgically on a large scale as a by-product in the roasting of ores containing arsenic. The trioxide thus formed volatilizes and is collected in walled chambers, in which it condenses in the form of a white powder (*white arsenic, poison flour*). To render it pure, it is again sublimed in iron cylinders, and obtained in the form of a transparent, amorphous, glassy mass (*arsenic glass*), the specific gravity of which equals 3.74. Upon preservation this variety gradually becomes opaque and porcelaneous, acquires a crystalline structure, and its specific gravity decreases to 3.69. Upon dissolving this oxide in hot hydrochloric acid, it crystallizes, on cooling, in shining, regular octahedra. At the same time, this interesting phenomenon is observed: that when the solution of the glass variety crystallizes it phosphoresces strongly in the dark, while the porcelaneous does not exhibit this property. Arsenic trioxide crystallizes in similar forms of the regular system when its vapors are rapidly cooled, but upon cooling slowly, it assumes the shape of monoclinic prisms of specific gravity 4.0; therefore it is dimorphous. When heated in the air, it sublimes above

218°, without melting; under higher pressure, however (in sealed tubes), it melts to a liquid which solidifies to a glassy mass.

The molecular magnitude of the solid arsenic trioxide, like that of all solids, is not known. When converted into vapor it behaves like sulphur and other solid liquid bodies; in vapor form at lower temperatures the molecules contain more atoms than at higher temperatures. According to Biltz (Z. f. phys. Ch. 20 (1896), 68), at temperatures ranging from 500° to 700° the molecules of As_4O_6 predominate, while between 700° and 1800° the molecules of As_2O_3 increase in number. Above 1800° the density corresponds to the old formula As_2O_3, and for this reason and simplicity's sake it is retained in the text. It is interesting to observe that at lower temperatures the same group As_4 is present in the molecule of arsenious oxide as was observed in the molecule of arsenic (p. 143).

The trioxide dissolves with difficulty in water; the solution possesses a sweetish, unpleasant metallic taste, exhibits but feeble acid reaction, and is extremely poisonous. The oxide is very soluble in acids, and probably forms salts with them; at least, on boiling, a solution of the trioxide volatilizes in strong hydrochloric acid, arsenious chloride, $AsCl_3$. From this and its feeble acid nature we perceive an indication of the basic character of the trioxide corresponding to the already partly metallic nature of arsenic (see p. 148).

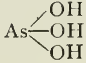
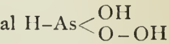
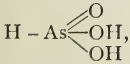
Nascent hydrogen converts the trioxide into arsine (AsH_3); but when heated with charcoal it is reduced to the metallic state (pp. 143, 144). Upon heating arsenic trioxide in a narrow glass tube with carbon, the reduced arsenic deposits as a metallic mirror on the sides. Oxidizing agents convert arsenic trioxide into arsenic acid.

Arsenious Acid, H_3AsO_3, corresponding to the anhydride, is not known in a free condition. It probably exists in the aqueous solution of arsenic trioxide, but the anhydride separates out upon evaporation. In its salts (*arsenites*) it is tribasic and usually affords tertiary derivatives:

$$Ag_3AsO_3, \quad Mg_3(AsO_3)_2.$$

The alkali salts, soluble in water, absorb oxygen from the air and serve as powerful reducing agents, they themselves becoming arseniates. Silver nitrate forms a yellow-colored precipitate, Ag_3AsO_3, with the soluble salts. [See Stavenhagen, Jr. f. prakt. Chem. 51 (1894), 1].

Other salts exist which are derived from the meta-arsenious acid, $HAsO_2$ (p. 201).

According to Klinger, arsenious acid, like sulphurous and phosphorous acids, is present in its derivatives in two forms: (1) the symmetrical  $As\begin{matrix}\diagup OH\\ -OH\\ \diagdown OH\end{matrix}$, from which the silver salt, the chloride and the esters are derived, and (2) the unsymmetrical  $H{-}As<^{OH}_{O-OH}$ or  $H-As\begin{matrix}/\!\!/ O\\ -OH\\ \diagdown OH\end{matrix}$, from which the alkali salts and alkyl arsonic acids (see Organic Chemistry) have their origin.

Arsenic Acid, H_3AsO_4 (*Acidum arsenicum*), is obtained by the oxidation of arsenic or its trioxide with concentrated nitric acid or by means of chlorine. Upon evaporating the solution rhombic crystals of the formula $H_3AsO_4 + \frac{1}{2}H_2O$ separate out; these deliquesce on exposure to the air. They melt at 100°, lose their water of crystallization and yield ortho-arsenic acid, H_3AsO_4, which heated to 140–180° passes into *Pyro-arsenic acid*, $H_4As_2O_7$:

$$2H_3AsO_4 = H_4As_2O_7 + H_2O.$$

At 200° this again loses water and becomes *Meta-arsenic acid*, $HAsO_3$. With water the last two acids become ortho- again; hence the latter is perfectly analogous to phosphoric acid. A portion of the arsenic acid is volatilized, probably as arsenious chloride, when strong hydrochloric acid solutions of arsenic acid are heated.

At a red heat the meta-arsenic acid loses all its water and becomes *Arsenic pentoxide*, As_2O_5, a white, glassy mass. Very strong ignition decomposes this into arsenic trioxide and oxygen; in contact with water it gradually changes to arsenic acid.

Ortho-arsenic acid is readily soluble in water, and is a strong tribasic acid. Its salts—the *arseniates*—are very similar to the phosphates and are isomorphous with them. With the soluble salts silver nitrate gives a reddish-brown precipitate of tri-silver arseniate, Ag_3AsO_4.

COMPOUNDS OF ARSENIC WITH SULPHUR.

Arsenic, like nitrogen and phosphorus, combines in several proportions with sulphur: *realgar*, As_2S_2, *auripigment* or *trisulphide*, As_2S_3, and *pentasulphide*, As_2S_5. They can be prepared by fusing arsenic and sulphur together. The two containing the more sulphur may be also obtained by passing hydrogen sulphide into solutions of the arsenic oxides. This indicates the metallic nature of arsenic, for this is the universal method of preparing metallic sulphides:

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O; \; As_2O_5 + 5H_2S = As_2S_5 + 5H_2O.$$

Arsenic Trisulphide, As_2S_3, occurs in nature as *auripigment* in brilliant yellow, leafy, crystalline masses of specific gravity 3.4. It is precipitated from acidulated solutions of arsenious acid or its salts by hydrogen sulphide, as a lemon-yellow amorphous powder. It is insoluble in water, but dissolves readily in ammonium hydroxide, the alkalies and alkaline sulphides. It is worthy of note that it dissolves upon prolonged heating in concentrated hydrochloric acid:

$$As_2S_3 + 6HCl = 2AsCl_3 + 3H_2S;$$

the arsenious chloride then volatilizes with the hydrochloric acid vapors.

Arsenic Pentasulphide, As_2S_5, separates as a bright yellow powder from the solution of sodium sulpharseniate, Na_3AsS_4 (see below), upon the addition of acids. Also if a rapid current of hydrogen sulphide be conducted through a slightly acidulated arsenic acid or arseniate solution, heated to 80°; the arsenic acid is then, according to R. Bunsen, slowly but completely converted into pentasulphide:

$$2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O$$

[Ann. Chem. **192** (1878), 305]. Under other conditions arsenic acid can be reduced by hydrogen sulphide entirely or in part to arsenious acid with the separation of sulphur:

$$H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S,$$

which is then either precipitated as trisulphide in the heat or in the presence of much hydrochloric acid it may be volatilized. Consult Brauner and Tomiček, Monatshefte f. Chem. VIII (1887), 607; McCay, Z. f. analyt. Chem. **27** (1888), 632, and Piloty and Stock, Ber. **30** (1897), 1649, upon the complex and as yet unexplained relations.

Arsenic Disulphide, As_2S_2, also exists. It occurs in nature as *realgar*, forming the beautiful, ruby-red crystals, of specific gravity 3.5. It is applied as a pigment. It is prepared artificially by fusing arsenic with sulphur in the proportion by weight expressed by its formula.

Arsenic Sulpho-salts.—Just as the oxygen compounds of arsenic combine with basic oxides and hydroxides to form salts, so the sulpho-salts are formed by combination of the arsenic sulphides with alkaline sulphides:

$$As_2S_3 + 3K_2S = \underset{\substack{\text{Tripotassium} \\ \text{sulpharsenite.}}}{2K_3AsS_3}$$

$$As_2S_5 + 3K_2S = \underset{\substack{\text{Tripotassium} \\ \text{sulpharseniate.}}}{2K_3AsS_4.}$$

For the preparation of these sulpho-salts, arsenic sulphide is dissolved in the aqueous solution of the alkaline sulphides or hydrogen sulphide is conducted through the alkaline solution of the oxygen salts:

$$K_3AsO_4 + 4H_2S = K_3AsS_4 + 4H_2O.$$

The sulpho-salts of the alkalies and ammonium are easily soluble in water, and when the solution is evaporated they generally separate in crystals. Acids decompose them, arsenic sulphide separating out and hydrogen sulphide becoming free:

$$2K_3AsS_4 + 6HCl = As_2S_5 + 6KCl + 3H_2S.$$

The silver salt, Ag_3AsS_3, silver sulpharsenite, is the mineral *proustite.*

Antimony, carbon, tin, gold, platinum and some other metals form sulpho-salts similar to those of arsenic (and of phosphorus).

4. OXYGEN COMPOUNDS OF ANTIMONY.

The oxygen derivatives of antimony are analogous in constitution to those of arsenic: antimony trioxide, Sb_2O_3, and antimony pentoxide, Sb_2O_5. The similarity of the two metals is indicated here just as in their chlorides. The trioxide does not possess acid but basic properties almost solely; it is true that a few salt-like compounds with such powerful bases as caustic soda and potash are known, but they are immediately decomposed by water with the separation of antimony trioxide oxide. Its salts with strong acids, in which it appears as a base, are also easily decomposed by water. The normal hydrate, H_3SbO_3, corresponding to arsenious acid, H_3AsO_3, may be obtained from potassium antimonyl tartrate (see Organic Chemistry). Other hydrates are not definitely known.

The higher oxidation product, the pentoxide, Sb_2O_5, on the contrary, has an acid nature and yields salts with the bases. The hydrate, H_3SbO_4, or ortho-antimonic acid, passes at 175° into *meta-antimonic acid*, $HSbO_3$, and at 275° into the *anhydride*, Sb_2O_5. Most of the antimoniates are derived from pyro-antimonic acid, $H_4Sb_2O_7$, which is produced on decomposing antimony pentachloride with water and drying the precipitate at 100° (p. 148).

Antimony Oxide (antimony trioxide), Sb_2O_3 or Sb_4O_6, is obtained by burning the metal in the air, or by oxidizing it with dilute nitric acid. By sublimation it may be obtained in two different crystal systems, in regular octahedra and in rhombic prisms. In these forms it occurs also in nature as the isometric *senarmontite* and rhombic *valentinite*. It is not isodimorphous with arsenic trioxide, which was long considered to be the case. Its vapor density at 1560° corresponds to the formula Sb_4O_6, and at higher temperatures it is very probable that it will be like arsenic trioxide, the simpler molecule Sb_2O_3. The hydrate, $Sb(OH)_3$, is thrown out as a white precipitate on adding dilute sulphuric acid to a solution of tartar emetic. It parts with water quite readily and changes to antimony trioxide also called antimonious acid.

The latter and the hydrate dissolve in sodium and potassium hydroxide, and, very probably, form salts ($NaSbO_2$) which decompose upon evaporating the solution. In this behavior the acid nature of antimony hydrate is also seen; therefore it has received the name of antimonious acid.

The oxide forms salts with acids, which are derived either from the normal hydrate, H_3SbO_3, or from the hydrate, $HSbO_2 = SbO.OH$ (*meta-antimonious acid*). In the salts of the first kind we have three hydrogen atoms of the hydrate replaced by acid radicals, or, what is the same, a trivalent antimony atom displacing three hydrogen atoms of the acids:

$$SbO_3(NO_2)_3 \text{ or } Sb(NO_3)_3.$$

Antimony nitrate.

In the second variety of antimony salts derived from the hydrate, SbO.OH, hydrogen is replaced by a univalent acid residue, or the hydrogen of the acid is substituted by the univalent group, SbO, known as *antimonyl*:

$$SbO.O.NO_2 \text{ or } NO_3(SbO).$$

Antimonyl nitrate.

Of these salts may be mentioned the following:

Antimony Sulphate, $Sb_2(SO_4)_3$, which separates when a solution of the oxide in concentrated sulphuric acid is cooled.

Antimonyl Sulphate, $(SbO)_2SO_4$, is formed when antimony oxide is dissolved in somewhat dilute sulphuric acid, and crystallizes in fine needles on cooling. Water decomposes both, forming basic salts; hence the basic nature of antimony oxide is slight.

Antimonic Acid, H_3SbO_4, is obtained upon warming antimony with concentrated nitric acid or by adding antimony pentachloride to cold water:

$$2SbCl_5 + 8H_2O = 2H_3SbO_4 + 10HCl.$$

It is most conveniently prepared by decomposing its potassium salt with nitric acid. It forms, when dried over concentrated sulphuric acid, a white powder of the composition indicated by the formula. When air-dried it has the formula—

$$2H_3SbO_4 + H_2O.$$

It is almost insoluble in water and in nitric acid, but reddens blue litmus-paper. It is a weak monobasic acid, the salts of which are mostly insoluble in water. [See Beilstein and v. Blaese, Chem. Centralblatt, 1889, 1, 803; Ebel, Ber. 22 (1889), 3044. See also p. 225.]

At 400° antimonic acid yields **antimony pentoxide,** Sb_2O_5, a yellow, amorphous mass, soluble in hydrochloric acid. At 800° the pentoxide breaks down into oxygen and the oxide, Sb_2O_4, which can be viewed as antimonyl meta-antimoniate ($SbO_3 . SbO$), or as a mixed anhydride, $\left.\begin{matrix} SbO \\ SbO_2 \end{matrix}\right\} O$. It is a white powder, becoming yellow when heated and at the melting point of silver is decomposed into oxygen and the trioxide.

COMPOUNDS OF ANTIMONY WITH SULPHUR.

These are perfectly analogous to the sulphur compounds of arsenic, and form sulpho salts with alkaline sulphides, corresponding to the oxygen salts. Acids precipitate antimony sulphide and liberate hydrogen sulphide from the sulpho-salts.

Antimony Trisulphide, Sb_2S_3, is found in nature as stibnite (*Stibium sulphuratum nigrum*) in radiating crystalline masses of dark-gray color and metallic luster; its specific gravity is 4.7. When heated it melts and distils. The artificial sulphide obtained by precipitating a solution of the oxide with hydrogen sulphide, is an amorphous red powder. When it is digested with aqueous hydrochloric acid or when carefully heated alone in an atmosphere of carbon dioxide it passes into the black, crystalline variety. Upon warming, the sulphide dissolves in concentrated hydrochloric acid to form antimony trichloride.

The compound, Sb_2S_2O, occurring in nature as red stibnite, can be artificially prepared, and serves as a beautiful red pigment, under the name of *antimony cinnabar*. *Kermes minerale*, employed in medicine, is obtained by boiling antimony sulphide with a sodium carbonate solution, and is a mixture of antimony trisulphide and antimony trioxide.

Antimony Pentasulphide, Sb_2S_5, or gold sulphur (*Stibium sulphuratum aurantiacum*), is precipitated by hydrogen sulphide from acid solutions of antimonic acid; it is more conveniently obtained by the precipitation of sodium sulphantimoniate, Na_3SbS_4, with hydrochloric acid:

$$2Na_3SbS_4 + 6HCl = Sb_2S_5 + 6NaCl + 3H_2S.$$

It is an orange-red powder, like the trisulphide; it decomposes on being heated into antimony trisulphide and sulphur. It dissolves to antimony trichloride in strong hydrochloric acid, with separation of sulphur and liberation of hydrogen sulphide.

Sodium sulphantimoniate, Na_3SbS_4 (Schlippe's salt), results from boiling pulverized antimony trisulphide with sulphur and sodium hydroxide (p. 223). Upon concentrating the solution it crystallizes in large yellow tetrahedra containing nine molecules of water ($SbS_4Na_3 + 9H_2O$); exposed to the air it becomes covered with a brown layer of antimony pentasulphide. It serves principally for the preparation of the officinal gold sulphur.

VANADIUM. NIOBIUM. TANTALUM.

$V = 51.2$. $Nb = 94$. $Ta = 183$.

The three rare elements, vanadium, niobium and tantalum, are closely related to the phosphorus group. They yield derivatives very much like those of the phosphorus group, but possess a more metallic character. They exhibit many characteristics similar to those of chromium, iron and tungsten, with which they are frequently associated in their naturally occurring compounds (compare the Periodic System of the Elements).

Vanadium, observed in 1801 by Del Rio and considered to be chromium until Sefström in 1830 proved it to be a new element, occurs in nature principally in the form of salts of vanadic acid (vanadium lead ore). Creuzot has recently worked the Thomas slags for vanadic acid, which originally was present in the iron ores. Vanadium may be obtained free by igniting its chlorides in a current of hydrogen. It is a grayish-white, metallic, lustrous powder, of specific gravity 5.5. It is difficultly fusible, and changes in the air very slowly at ordinary temperature. When heated, it burns to vanadium pentoxide, V_2O_5. It unites readily with nitrogen to form vanadium mononitride, VN.

Vanadium trichloride, VCl_3, forms red plates, which readily deliquesce in the air; it is not volatile.

Vanadium oxychloride, $VOCl_3$, results on heating a mixture of vanadium trioxide, V_2O_3, and carbon in chlorine gas. It is a lemon-yellow liquid, of specific gravity 1.84, and boils at 126°. It fumes strongly in the air and decomposes with water (analogous to phosphorus oxychloride) into vanadic acid and hydrochloric acid. Its vapor density corresponds to the formula $VOCl_3$.

Vanadium trioxide, V_2O_3, is a black powder obtained by heating vanadium pentoxide, V_2O_5, in hydrogen. It combines with oxygen, to form vanadium pentoxide, V_2O_5. The corresponding sulphate, $V_2(SO_4)_3$, combines, like the similarly constituted sulphates of aluminium, iron and chromium, with the sulphates of the alkalies to form alums (see these).

Vanadium pentoxide, V_2O_5, or vanadic anhydride, is a brown mass obtained by fusing the naturally occurring vanadates with niter, etc. It exists in three varieties. It is soluble in the alkalies, and forms with the metals salts of *vanadic*, H_3VO_4, and *metavanadic* acids, HVO_3. All these compounds are similar in constitution to those of the elements of the phosphorus group. In addition to these, vanadium forms other compounds, constituted like those of sulphur and chromium. In this class belong VCl_2 (dichloride), the tetrachloride, VCl_4, vanadious oxide, VO, vanadium dioxide, VO_2, and the oxychloride, $VOCl_2$. The tetrachloride, VCl_4, is a red-brown liquid, boiling at 154°; its vapor density corresponds to its formula.

Niobium, Nb, and **tantalum**, Ta, are not well known in the free state. They occur together as niobates and tantalates in a few rare minerals—the columbites and tantalites. The chlorides, $NbCl_5$ and $TaCl_5$, are volatile and are decomposed by water. Niobium and tantalum unite with potassium fluoride, forming double salts, *e.g.*, $2KFl.NbFl_5$ and $2KFl.TaFl_5$; also $2KFl.NbOFl_3$ and $2KFl.TaOFl_3$. When potassium niobium fluoride, $2KFl.NbFl_5$, is heated with sodium, *niobium hydride*, NbH, is formed. This is a grayish-black powder, which when heated burns to niobic anhydride, Nb_2O_5, and water. The oxides, Nb_2O_5 and Ta_2O_5, form salts of niobic (H_3NbO_4) and tantalic (H_3TaO_4) acids with bases.

---

4. OXYGEN DERIVATIVES OF THE ELEMENTS OF THE CARBON GROUP.

The following normal hydroxides correspond to the halogen derivatives, CCl_4, $SiCl_4$, $GeCl_4$, and $SnCl_4$, of the quadrivalent elements carbon, silicon, germanium, and tin (see p. 164):

$\overset{IV}{C}(OH)_4$	$\overset{IV}{Si}(OH)_4$	$\overset{IV}{Ge}(OH)_4$	$\overset{IV}{Sn}(OH)_4$.
Normal carbonic acid.	Normal silicic acid.	Normal germanic acid.	Normal stannic acid.

These normal hydrates or acids being true ortho-acids have but little stability, and exist chiefly in their derivatives. By the separation of one molecule of water, they pass into—

	CO_3H_2	SiO_3H_2	GeO_3H_2	SnO_3H_2,
Or				
	$CO(OH)_2$ Carbonic acid.	$SiO(OH)_2$ Silicic acid.	$GeO(OH)_2$ Germanic acid.	$SnO(OH)_2$. Stannic acid.

These hydroxyl derivatives deport themselves toward the normal just as the meta acids of the elements of the nitrogen group do to the ortho-acids (see p. 201). They constitute the ordinary acids of the quadrivalent elements carbon, silicon, germanium, and tin, and, as they contain two hydroxyl groups, are dibasic.

Carbon is the lowest member of this group, with the least atomic weight. Among the elements of the other three groups corresponding to it are nitrogen, oxygen, and fluorine:

$$C = 12 \qquad N = 14.04 \qquad O = 16 \qquad Fl = 19.$$

Fluorine and oxygen do not afford any oxygen acids. The normal acids of nitrogen, $N(OH)_5$ and $N(OH)_3$, are very unstable, and pass readily into the meta-acids, $NO_2.OH$ and $NO.OH$. The normal carbonic acid, $C(OH)_4$, corresponds to this, but is not capable of existing. Indeed, the meta- or ordinary carbonic acid, H_2CO_3, is also very unstable and at once decomposes, when separated from its salts, into water and carbon dioxide, CO_2. Even silicic, germanic, and stannic acids break down readily into water and their anhydrides:

CO_2 Carbon dioxide.	SiO_2 Silicon dioxide.	GeO_2 Germanium dioxide.	SnO_2. Tin dioxide.

1. OXYGEN COMPOUNDS OF CARBON.

Carbon Dioxide, CO_2, or carbonic anhydride (generally called carbonic acid), is produced when carbon or its compounds are burned in air or oxygen. It is found free in the air (in 100 volumes, on an average, 0.035 volumes CO_2), in many mineral springs (acid springs), and escapes in large quantities from the earth in many volcanic districts. It occurs in the liquid form, enclosed in the cavities of many crystalline minerals (quartz, topaz). It is prepared on a large scale by burning coke or by the ignition of limestone; in the laboratory it may be most conveniently obtained by the decomposition of calcium carbonate (marble or chalk) with dilute hydrochloric acid:

$$\underset{\text{Calcium carbonate.}}{CaCO_3} + 2HCl = \underset{\text{Calcium chloride.}}{CaCl_2} + CO_2 + H_2O.$$

Carbon dioxide is a colorless gas, with a slightly acid taste. Owing to its weight, the gas may be collected by air displacement, and may be poured from one vessel into another filled with air. A liter of carbon dioxide weighs 1.965 grams at 0°, 760 mm. pressure, and in 45° latitude at sea-level. By a pressure of 50–60 atmospheres at the ordinary temperature carbon dioxide can be liquefied, as was first shown by Faraday. The apparatus of Thilorier and Natterer were employed to this end. At present liquid carbon dioxide is brought into market enclosed in wrought-iron cylinders, and is used quite regularly in technical operations.

Carbon dioxide can only be liquefied below +30.9°; this is its critical temperature (p. 47). Its tension (critical pressure) at this point equals 77 atmospheres. If liquid carbon dioxide, enclosed in some suitable vessel, be allowed to escape into the air by opening a stop-cock (ordinary pressure), it immediately solidifies (see below) to a white, snowy mass. This is because in the evaporation of a part of the liquid so much heat is withdrawn that the remainder becomes solid. Solid carbon dioxide is a very poor conductor of heat and vaporizes very slowly. Notwithstanding its low temperature it can be handled without serious result, because it is always surrounded by a gaseous layer, and is, consequently, not in immediate contact with the skin. If, however, it be pressed between the fingers, it will produce painful burns.

The temperature of the solid carbon dioxide vaporizing in the air under ordinary pressure is about —78° (its boiling point). When the solid dioxide is mixed with a little ether it forms a paste, and then conducts heat better, and is, therefore, well adapted as a cooling agent. *In vacuo* its temperature diminishes to —140°.

Liquid carbon dioxide is a colorless, very mobile liquid. Its specific gravity is 0.91 at —1.6°, 0.84 at +15°, and 0.726 at +22.2°. Its coefficient of expansion is, consequently, greater than that of the gases; other gases behave similarly, but only such as are condensed under great pressure. If liquid carbon dioxide, contained in a glass tube, be heated, it expands rapidly and suddenly passes, at the critical temperature, +30.9°, into gas. This behavior enables us to determine without difficulty whether the liquids contained (see above) in minerals are liquid carbon dioxide.

If liquid carbon dioxide, confined in a glass tube, be cooled by a mixture of solid, snowy dioxide and ether (see above), it will solidify to a transparent ice-like mass, which will melt at —65°, according to another authority at —57°.

The tension of the solid or liquid dioxide, which at the same time indicates the pressure necessary for condensation at various temperatures, is given in the following table:

TEMPERATURE.	TENSION.	TEMPERATURE.	TENSION.
+30.9°	77 atmos.	—20°	19.9 atmos.
20°	58.0 "	—40°	10.2 "
10°	46.0 "	—60°	3.9 "
0°	35.4 "	—70°	2.1 "
		—80°	1.0 "

At the temperature of fusion of the solid dioxide (—65°) the tension equals about 3.5 atmospheres; the resulting liquid has this tension at this temperature. If the external pressure exerted upon it be less, it cannot exist as a liquid, but must immediately pass into the gaseous state. Herein we observe why the solid dioxide (under ordinary pressure) does not melt in the air, but vaporizes at once; and further, it explains why the liquid dioxide, subjected to the ordinary atmospheric pressure, cannot continue in this state—why it is either gasified at once or changed to the solid form.

Many other fusible solids behave like the dioxide. If the tension of their vapors at the fusion temperature exceeds that of the external atmospheric pressure they do not melt in the air, because the resulting liquid is immediately transformed into vapor; they vaporize (sublime) directly, without previous fusion. Such bodies are, *e. g.*, arsenic, arsenic trioxide, As_2O_3, camphor, mercurous chloride, HgCl, etc. They can be fused only under increased pressure (in sealed tubes). Again, all solids fusible in the air (under ordinary pressure) may be converted directly into gases by removing the external pressure. Thus iodine fuses at 114°, but sublimes in a vacuum without previous fusion. Mercuric chloride, $HgCl_2$, fuses at 265°, but not if the external pressure be less than 420 mm. Water melts at 0°, its tension at this temperature is 4.6 mm. If the external pressure be less (*in vacuo*), it will no longer melt, but vaporize at once. The pressure below which solids no longer melt has been called their *critical pressure* (Carnelley). It is, of course, understood that this is nothing more than the tension of the substance at its point of fusion.

Water dissolves an equal volume of the gas at 14°; at 0° it takes up 1.79 volumes. This proportion remains constant for every pressure, *i. e.*, at every pressure the same volume of gas is absorbed. As gases are condensed in proportion to the pressure, the quantity of absorbed gas is also proportional to the former (law of Henry and Dalton). Hence 1 volume of water absorbs, at 14° and 2 atmospheres pressure, 2 volumes, at 3 atmospheres 3 volumes, etc., of carbon dioxide—measured at ordinary pressure. The gas absorbed at higher pressure escapes with effervescence of the liquid when the pressure is diminished; upon this depends the sparkling of soda water and champagne, which are saturated with carbon dioxide under high pressure. Every naturally occurring water, especially spring water, holds carbon dioxide in solution, which imparts to it a refreshing taste.

As the product of a complete combustion carbon dioxide is not combustible, and is unable to support the combustion of most bodies; a glimmering chip is immediately extinguished in it. In a similar manner it is irrespirable. Although it is not poisonous, in the true sense of the word, yet the admixture of a few per cent. of carbon dioxide to the air makes it suffocating, as it retards the elimination of the same gas from the lungs.

It is decomposed by the continued action of the electric spark into carbon monoxide (CO) and oxygen; upon heating to 1300° it suffers a partial decomposition into carbon monoxide and oxygen. It is also decomposed when conducted over heated potassium or sodium, with separation of carbon; the potassium combines with oxygen to form potassium oxide:

$$CO_2 + 2K_2 = C + 2K_2O,$$

which forms potassium carbonate (K_2CO_3), with the excess of carbon dioxide. Glowing carbon reduces the dioxide to the monoxide (p. 231). Carbon monoxide is analogously formed on conducting a mixture of the dioxide and hydrogen (equal volumes) through a tube heated to redness, but between 250° and 300° the opposite reaction takes place, although only to a slight degree:

$$CO_2 + H_2 \rightleftarrows CO + H_2O.$$

The composition of carbon dioxide is readily determined by burning a weighed quantity of pure carbon (diamond or graphite) in a current of oxygen, and ascertaining the weight of the resulting gas. From the formula CO_2 it follows that in one volume of carbon dioxide there is contained an equal volume of oxygen. We may satisfy ourselves of this by burning carbon in a definite volume of oxygen; after cooling, there is obtained an equal volume of carbon dioxide:

$$C + \underset{\text{1 vol.}}{O_2} = \underset{\text{1 vol.}}{CO_2}.$$

The experiment is most practically executed by aid of the apparatus of Hofmann pictured in Fig. 66. The sphere-shaped expansion of the eudiometer limb of the U-tube is closed by means of a glass stopper, through which two copper wires pass. The one wire bears a combustion spoon at its end, upon which lies the carbon to be burned, while the other terminates in a thin piece of platinum, which is in contact with the carbon. For the performance of the experiment, the U-tube is filled, to near the bulb, with mercury and the air is expelled from the bulb limb by means of a rapid current of oxygen, the stopper made air-tight, the mercury level noted, and then pass the induction spark between the platinum wire and the copper spoon; this induces the burning of the carbon. As the volume of the enclosed gas is greatly expanded by the heat developed, it is advisable, in order to avoid the jumping out of the stopper, to previously reduce the pressure of the gas about two-thirds, by running out mercury. When the combustion is finished the mercury which was drawn off is returned and it rapidly assumes its original position. The same apparatus can also be employed for the illustration of the volume relations observed in the combustion of sulphur and other bodies.

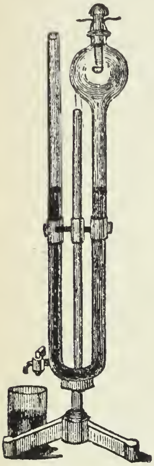


FIG. 66.

In dry condition, carbon dioxide, like all anhydrides, exhibits neither basic nor acid reaction. In aqueous solution it colors blue litmus-paper a faint red; upon drying the paper the red disappears, in consequence of the evaporation of the carbon dioxide.

We may then regard it as probable that free *carbonic acid*, H_2CO_3, is contained in the aqueous solution, but this readily decomposes into the dioxide, CO_2, and water. The salts of carbonic acid are produced by the action of carbon dioxide upon the bases:

$$2KOH + CO_2 = \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} + H_2O.$$

Carbon dioxide is, therefore, easily absorbed by potassium and sodium hydroxide. On conducting it through a solution of calcium or barium hydroxide, a white precipitate of barium or calcium carbonate, $BaCO_3$ or $CaCO_3$, is produced.

Carbonic acid is dibasic, forming primary (acid) and secondary (neutral) salts, $KHCO_3$ and K_2CO_3, called *carbonates*. As the acidity of carbonic acid is only slight, the secondary salts, obtained from strong bases, exhibit a basic reaction. Most acids expel the weak carbonic acid from its salts, with decomposition into carbon dioxide and water.

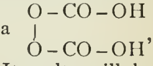
In the reduction of carbon dioxide we meet an interesting transition or transformation of substances of mineral origin into those of animate nature. According to Lieben nascent hydrogen readily reduces carbon dioxide in the form of dissolved bicarbonates to formic acid (formates):

$$\underset{\text{Sodium bicarbonate.}}{HO.COONa} + H_2 = \underset{\text{Sodium formate.}}{H.COONa} + H_2O.$$

And the latest researches show that water and hydrogen, under the influence of the silent electric discharge, reduce carbon dioxide to formic acid:

$$CO_2 + H_2 = H.COOH \text{ and } CO_2 + H_2O = H.COOH + O.$$

The reduction of carbon dioxide by the chlorophyl granules of plants in the sunlight is particularly important. It is by them that the almost endless number of "organic bodies" contained in plants is built up. In the animal organism, on the other hand, carbon dioxide and water are the chief decomposition products of organic compounds; consequently the exhaled air is rich in this acid.

Percarbonic acid, $H_2C_2O_6$, has been obtained by the electrolysis of acid carbonates just as persulphuric acid was formed from sulphuric acid. It is due to the union of the ions—O–CO–Me (Me = metal). The free acid would have the formula  $\begin{matrix}O-CO-OH\\ |\\ O-CO-OH\end{matrix}$, and may be said to be derived from hydrogen peroxide (p. 198). Its salts will be described later.

Carbon Monoxide, CO. Carbon dioxide is the first product in the combustion of coal. But just as soon as the combustion reaches a certain temperature—maximum—the excess of carbon reduces the dioxide and carbon monoxide is formed:

$$\underset{\text{1 vol.}}{CO_2} + C = \underset{\text{2 vols.}}{2CO}.$$

This is demonstrated by the following experiment: When dry air is conducted over heated coal, carbon dioxide is formed almost exclusively from 400° to about 700°. From this point forward carbon monoxide appears in increasing amount and from 1000° upwards it is almost the sole product. Hence glowing coals at moderate temperature burn without flame, but at more elevated temperatures (from 1000° upwards) flame is present (p. 155).

Zinc-dust reacts like carbon:

$$CO_2 + Zn = ZnO + CO.$$

When carbon dioxide is conducted through a glass tube, containing zinc-dust heated to a faint red heat, almost pure carbon monoxide escapes. A more convenient procedure consists in heating pulverized magnesium carbonate and zinc-dust in a glass retort, when CO, containing CO_2, is eliminated; subsequently the former alone escapes. Pure monoxide is also formed upon heating zinc-dust with chalk (in equivalent quantities):

$$Zn + CaCO_3 = ZnO + CaO + CO,$$

a very convenient method for its preparation.

The monoxide is produced, further, by igniting carbon with different metallic oxides, *e. g.*, zinc oxide:

$$ZnO + C = Zn + CO.$$

Water is similarly decomposed. On conducting aqueous vapor over burning carbon there is produced a mixture of carbon dioxide and hydrogen:

$$C + 2H_2O = CO_2 + 2H_2.$$

By further action of the heated carbon the carbon dioxide in this equation is reduced to carbon monoxide. This gas mixture is known as *water gas* and is applied technically. [See A. Naumann, Ber. **25** (1892), 1, 556; also p. 229.]

A mixture of hydrogen and carbon monoxide is also produced when the electric arc passes between carbon points under water:

$$H_2O + C = CO + H_2.$$

For the preparation of carbon monoxide, oxalic acid is warmed with sulphuric acid; the latter withdraws water from the former, and the residue breaks down into carbon dioxide and monoxide:

$$H_2C_2O_4 = CO_2 + CO + H_2O.$$

The disengaged mixture of gases is conducted through an aqueous solution of sodium hydroxide, by which the carbon dioxide is absorbed, the monoxide passing through unaltered. Pure carbon monoxide may be prepared by heating yellow prussiate of potassium (see Iron) with 9 parts of concentrated sulphuric acid. The resulting gas is conducted through sodium hydroxide to remove from it traces of carbon dioxide and sulphur dioxide. Pure monoxide is also produced when concentrated formic acid or lead formate is heated with concentrated sulphuric acid:

$$CO_2H_2 = CO + H_2O.$$

A liter of the gas weighs 1.25078 grams under normal conditions; it is therefore 0.9672 as heavy as air. It is one of the gases which are condensed with difficulty. Its critical temperature is —141° and its critical pressure is 35 atmospheres. Liquid carbon monoxide solidifies under 100 mm. pressure at —207° and under 4 mm. pressure at —220° (Olszewsky). It boils at —190° under 760 mm. pressure. It is almost insoluble in water, but is readily dissolved by an ammoniacal solution of cuprous chloride (Cu_2Cl_2) with which it forms a crystalline compound, but this decomposes when its solution is heated and carbon monoxide is again liberated. When ignited, it burns in the air, with a faintly luminous, beautiful blue flame, which distinguishes it from other combustible gases. With air or oxygen, it affords (similar to hydrogen) a very explosive mixture:

$$\underset{\text{2 vols.}}{2CO} + \underset{\text{1 vol.}}{O_2} = \underset{\text{2 vols.}}{2CO_2}.$$

The union of carbon monoxide and oxygen takes place at very high temperatures; hence the burning flame of the gas is extinguished upon cooling. A flame or a spark from a powerful induction coil is necessary to ignite a *dry* mixture of carbon monoxide and oxygen. When the two gases are moist they are more easily ignited and combustible. This is explained by the fact that carbon monoxide unites with the aqueous vapor and yields the dioxide and hydrogen ($CO + H_2O = CO_2 + H_2$), which then combines with oxygen and forms water (pp. 101, 230).

In consequence of its ready oxidation, it is capable of reducing most metallic oxides at a red heat:

$$\underset{\text{(37.1 Cal.)}}{CuO} + \underset{\text{(28.5 Cal.)}}{CO} = Cu + \underset{\text{(96.9 Cal.)}}{CO_2} \ldots + (31.3\ \text{Cal.})$$

Some noble metals are precipitated from solutions of their salts by carbon monoxide even in the cold. Thus, palladium and gold are thrown out from their chloride solutions by it. A piece of paper moistened with palladious chloride ($PdCl_2$) is blackened by it (delicate test for CO). When carbon monoxide is conducted into a platinic chloride solution platinous chloride separates.

Carbon monoxide is reduced to carbon with difficulty. Burning bodies are extinguished by it. When heated with potassium it is decomposed with separation of carbon. Under the influence of the silent electric discharge hydrogen reduces it to formic aldehyde:

$$CO + H_2 = H.COH.$$

This is the simplest organic compound, consisting of carbon, oxygen and hydrogen. Water under like conditions changes carbon monoxide to formic acid:

$$CO + H_2O = H.COOH$$

(see p. 231).

When inhaled, even in slight quantity, it acts very poisonously. Blood containing carbon monoxide is characterized by very distinct spectrum reactions.

In 1890 L. Mond, in conjunction with other chemists, discovered an exceedingly remarkable property of carbon monoxide, viz., that it combined with very finely divided nickel at 25–30° to form a liquid, which volatilized readily—nickel carbonyl, $Ni(CO)_4$. Since then it has been observed that carbon monoxide also combines with other metals of the iron group, forming metal carbonyls.

Nickel Carbonyl, $Ni(CO)_4$, is a colorless, strongly refracting liquid, which boils at 43° (751 mm. pressure) and becomes crystalline at —25°.

Its vapors decompose with explosion at 60°; in the air they burn with a very smoky flame [see Z. f. phys. Ch. 8 (1891), 150].

Carbon monoxide, being an unsaturated compound, combines like ethylene (p. 154) with two atoms of chlorine to **Carbonyl Chloride** or **Phosgene Gas**, $COCl_2$, the chloride corresponding to carbonic acid:

$$\underset{\text{1 vol.}}{CO} + \underset{\text{1 vol.}}{Cl_2} = \underset{\text{1 vol.}}{COCl_2}.$$

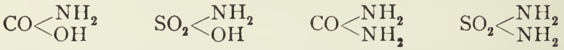
It is obtained by bringing together equal volumes of carbon monoxide and chlorine in direct sunlight (hence the name from φῶς, light, and γεννάω, I produce); also when the gases are conducted over ignited platinum sponge or animal charcoal. It can also be made by conducting monoxide into antimony pentachloride, $SbCl_5$.

This compound is important in the color industry, and other convenient methods for its preparation may be found by consulting Erdmann, Ber. **26** (1893), II, 1990.

It is a colorless, suffocating gas, the density of which agrees with the molecular formula $COCl_2$. Phosgene can easily be liquefied by chilling; it boils at +8° and has the specific gravity 1.43. Water decomposes it into hydrogen chloride and carbon dioxide:

$$COCl_2 + H_2O = CO_2 + 2HCl.$$

Amido-derivatives.—The following are amido-derivatives of carbonic acid which are fully treated in Organic Chemistry and will receive but mere mention here: *Carbamic acid*, $CO{<}\begin{smallmatrix}NH_2\\OH\end{smallmatrix}$, and *carbamide* or urea, $CO{<}\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}.$ They bear the same relation to carbonic acid that sulphamic acid and sulphamide sustain to sulphuric acid:



$$CO{<}\begin{smallmatrix}NH_2\\OH\end{smallmatrix} \qquad SO_2{<}\begin{smallmatrix}NH_2\\OH\end{smallmatrix} \qquad CO{<}\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix} \qquad SO_2{<}\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}$$

and can be obtained in a corresponding manner from carbonyl chloride and ammonia. Analogous bodies are derived from hydrazine—the *hydrazides*, e. g., *carbohydrazide*, $CO{<}\begin{smallmatrix}NHNH_2\\NHNH_2\end{smallmatrix}.$ Mention may also be made of *nitrogen carbonyl*, $CO{<}\begin{smallmatrix}N_3\\N_3\end{smallmatrix}$, prepared by Curtius and Heidenreich. It is the counterpart of phosgene but is obtained from hydrazoic acid. It is a very explosive, exceedingly volatile, crystalline compound. In this body also the group N_3 deports itself like the halogens. [See p. 133 and Ber. **27** (1894), 2684; Jr. prakt. Ch. **52** (1895), 454.]

COMPOUNDS OF CARBON WITH SULPHUR.

Carbon Bisulphide, CS_2, is formed, like the dioxide, by the direct union of carbon and sulphur; if vapors of the latter are led over ignited carbon the escaping bisulphide vapors are condensed in a cooled receiver. Pure carbon bisulphide is a colorless, mobile liquid, of faintly ethereal, and in no sense disagreeable, odor; it solidifies at —116°, and refracts light strongly. Its specific gravity equals 1.29 at 0°. It is very volatile, boils at 47°, and burns with a blue flame to carbon dioxide and sulphur dioxide. When a mixture of carbon bisulphide vapors and oxygen is ignited, a violent explosion ensues:

$$\underset{\text{1 vol.}}{CS_2} + \underset{\text{3 vols.}}{3O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{2 vols.}}{2SO_2}.$$

In nitric oxide, the vapors burn with an intensely brilliant flame. On directing a strong current of air upon carbon bisulphide in a porcelain capsule (which conducts heat poorly), so much heat is absorbed by the evaporation that the residual liquid solidifies to a white, snow-like mass which contains water. Carbon bisulphide is insoluble in water; but mixes, in every proportion, with alcohol and ether. It dissolves iodine with a violet-red color, and serves as an excellent solvent for sulphur, phosphorus, caoutchouc, and the fatty oils. On conducting carbon bisulphide vapors over heated zinc-dust, all the sulphur unites with the zinc, forming zinc sulphide, while the carbon separates as soot:

$$CS_2 + 2Zn = 2ZnS + C.$$

Most metals react in a similar manner.

Carbon bisulphide may be viewed as the anhydride of *sulphocarbonic acid*, H_2CS_3. The salts of this acid are obtained by the solution of carbon bisulphide in alkaline sulphides (see Sulpho-salts, p. 223):

$$CS_2 + K_2S = K_2CS_3.$$

On adding hydrochloric acid to the solutions of these salts the sulphocarbonic acid separates as a reddish-brown oil. This decomposes readily.

The sulphur compound corresponding to carbon monoxide is not known: there exists, however, one containing both oxygen and sulphur—**carbon oxysulphide**, COS. This substance is produced (in small quantity, because it decomposes at about the same temperature) when a mixture of sulphur vapors and carbon monoxide gas is passed through red-hot tubes.

It is most readily obtained from potassium sulphocyanide, CN.SK (see Organic Chemistry) by the action of dilute sulphuric acid. Carbon oxysulphide is a colorless gas, with an odor reminding one of hydrogen sulphide. It is present in some sulphur springs. The gas is very readily inflammable and burns with a blue flame to carbon dioxide and sulphurous acid.

It is soluble in an equal volume of water, decomposing gradually (more rapidly in the presence of alkalies) into the dioxide and hydrogen sulphide:

$$COS + H_2O = CO_2 + HS_2.$$

CYANOGEN COMPOUNDS.

Of the compounds of carbon mention will also be made of those of cyanogen, as they are of importance in inorganic chemistry.

Nitrogenous carbon compounds heated with potassium hydroxide yield potassium cyanide, KCN, which with ferrous oxide forms the so-called yellow prussiate of potassium, $K_4Fe(CN)_6$. All the other cyanogen derivatives may be prepared from these two compounds. They all contain the group CN, called *cyanogen*. It is similar to the groups OH, NH_2, CH_3, and is a univalent radical (pp. 167, 171). In chemical behavior the cyanogen group is very similar to the halogens and the group N_3 of hydrazoic acid; with the metals it forms metallic cyanides (KCN, AgCN) very similar to the haloid salts. Hydrogen cyanide is evolved when the cyanides are heated with sulphuric acid:

$$2KCN + H_2SO_4 = K_2SO_4 + 2HCN.$$

Hydrogen Cyanide, HCN, is a colorless, mobile liquid, of peculiar odor, and boiling at 27°. Like the halogen hydrides, it is an acid, forming salts with metals and bases, and is known as *hydrocyanic* or *prussic acid.* Both it and its salts are very powerful poisons. If the CN group is separated from its salts it doubles itself, yielding *dicyanogen* or *free cyanogen*, C_2N_2 ($N \equiv C - C \equiv N$), because, like the other univalent groups (as CH_3, see p. 168), it cannot exist in a free condition.

The heats formation of the simplest carbon compounds (from the diamond) above cited correspond with the symbols:

$$(C,O) = 26.3 \qquad (CO,O) = 68.3 \qquad (C,O_2) = 94.3 \qquad (CO_2,Aq) = 5.8.$$

If an element combine with another according to multiple proportions, there usually occurs, in the union of the first atom, a greater disengagement of heat than with the following atom. The numbers above, on the contrary, show that the union of the second atom of oxygen with carbon (CO,O) sets free 68.3 Cal.; that of the first atom (C,O), however, only 26.3 Cal. This can only be explained by the fact that, for the vaporization and disaggregation of the solid carbon molecules, heat is necessary. If we assume that the direct union of the first atom also disengaged 68.3 Cal., it would follow from this that, in the dissociation of 12 parts by weight of carbon into gaseous free atoms, 42.0 (= 68.3 — 26.3) Cal. were absorbed.

2. OXYGEN COMPOUNDS OF SILICON.

Silicon Dioxide, SiO_2 (*Silica*), the only well-known oxide of silicon, is widely distributed in nature as rock-crystal, quartz, sand, etc. Quartz occurs in nature crystallized in figures of the hexagonal system, with the specific gravity, 2.6; these crystals are colorless, or colored by impurities.

Quartz is a very widely distributed mineral. The following varieties, distinguished by color and general appearance, exist: Rock-crystal, colorless; smoky quartz, brown; morion, almost black; citrine, yellow; amethyst, violet, which on heating becomes yellow. Common quartz is cloudy, slightly transparent, white or colored. It is an essential constituent of granite, gneiss, quartz-porphyry, sandstone and other rocks. Special varieties of it are: fibrous quartz (tiger's-eye, Africa), the cat's-eye (Ceylon), etc. The gray hornstone, the green chrysoprase and red or brown jasper consist of compact quartz, etc.

Tridymite (τρίδυμοι, triplets) has the same composition as quartz and crystallizes in the hexagonal system. It is found in volcanic rocks. Its specific gravity is 2.3.

Silica may be obtained in an amorphous form by igniting the silicic acid which separates from silicates, but in fusions it has been obtained in both crystalline forms. The natural anhydride always contains impurities; the purest is the colorless rock-crystal.

Silicon dioxide is insoluble in water and in all acids; but is decomposed by hydrofluoric acid with the formation of silicon fluoride ($SiFl_4$) and water (p. 162). Strong ignition with sodium or potassium reduces it in part to metallic silicon. The reduction is readily effected by the use of metallic magnesium or aluminium [Gattermann, Ber. **22** (1889), 186; Winkler, *ibid.* **23** (1890), 2652; Jahrb. f. Chem. v (1895), 88]:

$$SiO_2 + 2Mg = 2MgO + Si.$$

The dioxide prepared artificially dissolves when boiled with potassium or sodium hydroxide; the natural only when finely divided [Jahrb. f. Chem. VII (1897), 85]. By fusion with the hydroxides or carbonates of the alkalies all varieties of silica yield a glassy mass (water-glass) soluble in water and containing silicates (K_4SiO_4 or K_2SiO_3). Upon the addition of hydrochloric acid to the aqueous solution of the potassium or sodium salt, a very voluminous, gelatinous mass separates; this is probably *normal* or *orthosilicic acid*, H_4SiO_4:

$$Na_4SiO_4 + 4HCl = 4NaCl + H_4SiO_4.$$

Orthosilicic acid is also formed in the decomposition of silicon fluoride by water (p. 163). It becomes a white amorphous powder having the composition H_2SiO_3 or $3SiO_2 . 2H_2O$ when washed with water and dried in the air. By strong ignition water is gradually expelled until finally the anhydride remains. The freshly precipitated acid is somewhat soluble in water, more readily in dilute hydrochloric acid and in caustic soda. On adding a solution of sodium silicate to an excess of dilute hydrochloric acid the silicic acid remains dissolved. From the hydrochloric acid and sodium chloride solution we can obtain a perfectly pure aqueous solution of silicic acid by dialysis by proceeding in the following manner:

Pour the hydrochloric acid solution into a wide cylindrical vessel, *a*, *a*, whose lower opening is covered with animal bladder or parchment paper, and then suspend the vessel (dialyser) in another, *b*, containing pure water (Fig. 67). Osmosis now sets in. The sodium chloride and hydrochloric acid pass through the parchment paper into the outer water, *b*, while on the other hand, water passes from the outer vessel into the dialyser; the parchment paper is not permeable to silicic acid. This alternate diffusion of the different particles occurs until the outer and inner liquids show the same quantity of diffusible substances. Upon introducing the dialyser into a fresh portion of water, the dialysis commences anew. Finally, after repeated renewal of the external water, the dialyser will contain a perfectly pure silicic acid solution, free from sodium chloride and hydrochloric acid. The solution may be concentrated by evaporation; it then readily passes into a

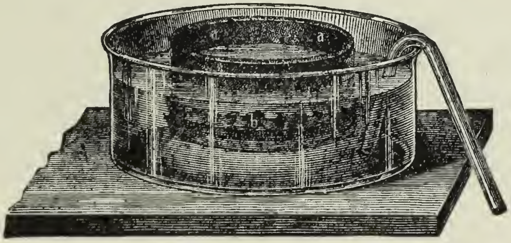


FIG. 67.

gelatinous mass. The same occurs instantaneously in dilute solutions if a trace of sodium carbonate be added or carbon dioxide be led into it.

Like sodium chloride, all crystallizable soluble substances diffuse through parchment. These are known as *crystalloids*, to distinguish them from the non-diffusible *colloids*. To the latter belong gum, gelatine, albumin, starch, glue (κόλλα, hence the name colloid), and especially most of the substances which occur chiefly in vegetable and animal organisms. Like silicic acid these colloids exist in liquid, soluble, and solid gelatinous conditions. Many other substances (like ferric and aluminium oxides) which ordinarily are insoluble in water, can be brought into aqueous solution by dialysis.

For "osmotic pressure" and the determination of molecular weights see Solutions.

We have already seen that acids like sulphuric, phosphoric, and arsenic, are capable of forming anhydro- or poly-acids by the union of several molecules and the elimination of water (p. 214). Silicic acid is particularly inclined to that form of condensation. It forms a large number of *poly-silicic acids*, $Si_2O_3(OH)_2$, $Si_3O_4(OH)_4$, $Si_3O_5(OH)_2$, etc., derived from the normal and ordinary acid, according to the common formula:

$$m\mathrm{Si(OH)_4} - n\mathrm{H_2O}.$$

These poly-acids are not known free; it appears, however, that many amorphous forms of silica occurring in nature, as agate, chalcedony, opal, which lose 5–15 per cent. of water by ignition, represent such poly-acids. The natural *silicates* are the salts of such acids. *Agate* consists of numerous layers of variously colored chalcedony, quartz and amethyst. The majority are derived from the acids $H_2Si_2O_5$, $H_4Si_3O_8$, $H_2Si_3O_7$, $H_4Si_4O_{10}$, and others. Only a few silicates are obtained from the normal acid, *e. g.*, chrysolite, Mg_2SiO_4.

Corresponding to carbon bisulphide, CS_2, is

Silicon Disulphide, SiS_2, which may be made by heating amorphous silicon with sulphur, or by conducting sulphur vapors over an ignited mass of silica and carbon. It sublimes in shining, silky needles, which water changes to silicic acid and hydrogen sulphide.

Germanium, Tin and **Lead** belong to the group of carbon and silicon. They yield the derivatives MeO_2 and $Me(OH)_4$ (pp. 226, 227), but as they form lower oxides, GeO and SnO, which manifest a perfectly basic nature and unite with acids to form salts, and as these elements are thereby allied to the metals, they will be discussed under that division.

TITANIUM. ZIRCONIUM. THORIUM.

Ti = 48.1. Zr = 90.6. Th = 232.

The same relation that vanadium, niobium, and tantalum show to the elements of the phosphorus group is manifested by the three elements titanium, zirconium and thorium for the silicon group (see Periodic System, p. 246).

P = 31.0	V = 51.2	Si = 28.4	Ti = 48.1
As = 75	Nb = 94	Ge = 72	Zr = 90.6
Sb = 120	Ta = 183	Sn = 118.5	Th = 232.

In all their deportments they strongly resemble tin; they possess, however, a more metallic character in their derivatives. They are quadrivalent, affording compounds of the form MeX_4, in which X represents univalent elements and groups; those of the form MeX_2, corresponding to the stannous derivatives, are unknown. The hydroxides, $Me(OH)_4$ and $MeO(OH)_2$, have a stronger basic nature than stannic acid and form stable salts with acids; the basicity increases successively with the atomic weights. Corresponding to this, the acidity of the hydrates, *i. e.*, their capability of exchanging hydrogen for metals, gradually diminishes. Thorium hydroxide, $Th(OH)_4$, is not able to form metallic salts.

TITANIUM.

Ti = 48.1.

This metal occurs in nature as titanium dioxide (rutile, anatase, brookite) and in titanates (perofskite, $CaTiO_3$, menaccanite, $FeTiO_3$). Free titanium is a gray, metallic powder, obtained by Berzelius on heating potassium titanium fluoride (K_2TiFl_6) with potassium. Wöhler, however, was the first to recognize it as metal. It burns when heated in the air, and decomposes water on boiling. It dissolves in dilute hydrochloric and sulphuric acids, with evolution of hydrogen.

Titanium Chloride, $TiCl_4$, is formed, like silicon chloride, by conducting chlorine over an ignited mixture of the dioxide and carbon. A colorless liquid, of specific gravity 1.76, fuming strongly in the air (with decomposition into hydrochloric and titanic acids), and boiling at 136°. It solidifies at —25°. The vapor density corresponds to the molecular formula $TiCl_4$. It behaves like tin tetrachloride with water. A compound—*hydrofluotitanic acid*, H_2TiF_6—and its salts are known. They correspond to hydrofluosilicic acid.

Titanic Acid, H_4TiO_4 (first obtained pure by H. Rose), separates as a white, amorphous powder, on adding ammonium hydroxide to the hydrochloric acid solution of the titanates. When dried over sulphuric acid it loses 1 molecule of water and becomes $TiO(OH)_2$. Titanic acid, like silicic and stannic acids, forms poly-acids. The hydrates dissolve in alkalies and strong acids, to form salts. On igniting the hydroxides we get

Titanium Dioxide, TiO_2, which may be procured crystallized as rutile, brookite, and anatase. When ignited in a stream of hydrogen it changes to the oxide Ti_2O_3. Titanium dioxide is almost insoluble in acids; it is only dissolved by hydrofluoric acid. It forms titanates upon fusion with the alkalies.

The hydroxides, TiO_4H_4, TiO_3H_2, etc., conduct themselves as feeble bases with strong acids and afford salts with them (*e. g.*, $TiO.SO_4$), which are decomposed by water. The alkaline titanates (K_2TiO_3) are very unstable. Other titanates occur in nature, *e. g.*, $CaTiO_3$, $MgTiO_3$, and the so-called titanic iron, $FeTiO_3$.

Titanium also forms derivatives after the types, Ti_2O_3 and TiO, *e. g.*, Ti_2Cl_6 and Ti_2Cl_4. The sesquioxide compounds are usually green or violet in color, while those of the monoxide form are black or brown.

Titanium yields various compounds with nitrogen. When the dioxide is heated in ammonia gas, a dark-violet powder of the composition TiN_2 results. The compound Ti_5CN_4—the so-called cyan-titanium nitride—is sometimes found in copper-red, metallic cubes, in blast-furnace slag, when iron ores, containing titanium, have been fused.

ZIRCONIUM.

Zr = 90.6.

Zirconium is very rare in nature, but is generally found in silicates, and especially as zircon, $ZrSiO_4$. Free zirconium, like carbon, is known in three allotropic forms. On fusing potassium zirconium fluoride with aluminium L. Troost obtained it in brilliant, hard, steel-gray, flat leaflets, of specific gravity 4.15, which burned in the oxyhydrogen flame to the dioxide. L. Troost also isolated the graphitic form. The amorphous variety was observed by Berzelius, who was the first chemist after Klaproth, its discoverer, to engage in a study of zirconium. He obtained it by the method used for titanium and got it as a black powder which burnt readily. Zirconium tetrachloride, $ZrCl_4$, and fluoride, $ZrFl_4$, are very similar to the corresponding titanium compounds.

Zirconic acid, $Zr(OH)_4$, is not definitely known. Metazirconic acid, $ZrO(OH)_2$, is precipitated on adding ammonia water to acid solutions, in the form of a white, voluminous mass, which yields zirconium dioxide, ZrO_2, upon ignition. A colorless, transparent crystalline modification is known—isomorphous with rutile and cassiterite. Metazirconic acid is insoluble in caustic potash and soda; it only forms zirconates, Na_2ZrO_3 and Na_4ZrO_4, when fused with alkalies and alkaline carbonates. Water decomposes these salts with the liberation of alkali. Freshly precipitated metazirconic acid, $ZrO(OH)_2$, dissolves readily in strong acids. Zirconium dioxide is soluble in hot, concentrated sulphuric acid, forming $Zr(SO_4)_2$, which can also be obtained from aqueous solution in crystals, $Zr(SO_4)_2 . 4H_2O$.

In late years zirconium dioxide has become of great importance for illuminating purposes. It is, therefore, prepared in large amounts from zircon. The finely pulverized mineral is mixed with carbon and while being gently heated chlorine is conducted over the mixture when silicon chloride, $SiCl_4$, and zirconium chloride, $ZrCl_4$, are produced; or the mineral is decomposed with hydrofluoric acid. Berzelius noticed the light-emission power of the oxide when it was heated. Caron (1868) determined its value for the temperature of the oxyhydrogen flame and Tessié du Mothay endeavored to utilize it practically. Linnemann (1885) made the oxide into thin plates and soon thereafter W. Kochs succeeded by a peculiar process in shaping it into any desired form. The durability of the zirconia light-giving bodies in the oxyhydrogen flame, the fact that they do not decompose in the air, that the light which they diffuse is intensely white (its continuous spectrum includes the Fraunhofer lines from A to H) render it superior to the Drummond lime light. It is extensively used for projection lamps, for photography and in optical researches.

THORIUM.

Th = 232.

Until recently thorium was only known as a constituent of certain rare northern minerals. Berzelius first discovered it in the thorite from Arendal, later Wöhler found it in pyrochlore, and Kersten in monazite. Small amounts of it are present in many orthites. Its application to illuminating purposes has created a demand for large quantities of it and at present it is isolated from a rich monazite deposit in McDowell County, N. C. That mineral contains 5.6 per cent. of thorium oxide.

Free thorium has been obtained as a gray, crystalline powder of specific gravity 11.0 by reducing potassium thorium fluoride or potassium thorium chloride with metallic sodium or potassium. Its specific heat is 0.0276. It burns, when heated in the air, to dioxide, thoria, ThO_2. The metal is easily soluble in concentrated sulphuric acid, nitric acid, and hydrochloric acid. It is not soluble in the alkalies. The tetrachloride, $ThCl_4$, results from the action of hydrogen chloride upon metallic thorium; it melts at a white heat and sublimes in white needles. Its vapor density corresponds to the formula $ThCl_4$. It is soluble in water and separates in crystals of the formula $ThCl_4 . 8H_2O$. It forms crystalline double salts with the alkaline chlorides. The fluoride, $ThFl_4$, is a white powder, insoluble in water. The hydroxide, $Th(OH)_4$, is precipitated as a white jelly on adding ammonia water to thorium salts. The hydroxide, $ThO(OH)_2$, is not known. On heating thorium hydroxide, $Th(OH)_4$, the dioxide, ThO_2, is obtained. The latter is not soluble in dilute acids; it is, however, converted into thorium sulphate, $Th(SO_4)_2$, when acted upon with concentrated sulphuric acid. The sulphate dissolves readily in cold water and crystallizes from the same in colorless, brilliant needles of the formula $Th(SO_4)_2 . 9H_2O$. When its aqueous solution is heated almost all of the sulphate separates as a woolly mass, which on cooling, slowly dissolves. The hydrate and dioxide do not form salts with the alkalies. The isomorphism of thorium dioxide with uranium dioxide, and thorium sulphate with uranium sulphate is very interesting.

Thorium dioxide is even more valuable for lighting purposes than zirconium dioxide because it gives forth a blinding light at the temperature of the Bunsen flame—light rays of every refrangibility are emitted. Auer von Welsbach has utilized this property in a gas-light. Fine-meshed material of cotton or linen saturated with a solution of thorium nitrate and a little cerium nitrate, surrounds the colorless flame of a Bunsen burner. When the vegetable material has burned away a mantel of thorium dioxide and cerium oxide remains, which has the exact form of the original substance, and emits a bright, clear, soft light. The ordinary "glow mantles" contain about 98–99 per cent of thoria and 2–1 per cent. cerium oxide; it is exactly this mixture which affords the desired white light. The intense emission power Bunte believes is due to the catalytic action of finely divided cerium oxide, which causes a rapid combustion and consequently a high temperature. Hence in the Welsbach mantle the thorium oxide simply acts as a stable, porous carrier for the cerium oxide.

BORON.

B = 11.

This element is generally classed with the metalloids, and stands isolated among them; it forms the transition from these to the metals, which is manifest from its position in the periodic system. On the one side, especially when free, it resembles carbon and silicon; on the other, it approaches the metals, beryllium, aluminium, and scandium (see the Periodic System of the Elements). As recently observed, it affords a gaseous hydride, but it is not very stable, and, like stibine, may be easily decomposed into its constituents. Its oxide, B_2O_3, although really of an acid nature, approaches such metallic oxides as aluminium oxide, Al_2O_3, which functionates both as base and acid. Boron is trivalent, and yields only compounds of the form BX_3.

It is found in nature as boracic acid and in the form of borates, like borax (sodium salt), boracite ($2Mg_3B_8O_{15} + MgCl_2$; Stassfurt). Boron exists in two allotropic modifications: amorphous and crystalline.

Moissan made *amorphous* boron by igniting a mixture of freshly fused boric acid with magnesium powder, free from iron. By a rather circuitous treatment of the fusion the boron (with 2 per cent. impurities) is obtained as a black powder of specific gravity 2.45. The product obtained heretofore by other methods, and believed to be amorphous boron, was a mixture of boron, iron boride, boron nitride, etc. The boron of Moissan ignites at 700° in the air; at higher temperatures sulphur, chlorine, bromine, nitrogen, silver and platinum combine readily with it. It has a great affinity for oxygen, hence acts as a powerful reducing agent. When rubbed together with lead dioxide explosion occurs. Oxygen acids are comparatively easily reduced by boron; potassium permanganate, silver nitrate and ferric chloride suffer this change in the cold.

The *crystalline* variety may be obtained by igniting boron trioxide with aluminium. The boron, separated by the aluminium, dissolves in the excess of the latter, and crystallizes from it on cooling; upon dissolving the aluminium in hydrochloric acid the boron remains in shining, transparent, quadratic crystals, which are more or less colored, and have a specific gravity of 2.63. The crystals are not pure boron, but contain aluminium and carbon. In their luster, refraction of light, and hardness, they resemble the diamond. Crystalline boron is more stable than the amorphous; it does not oxidize upon ignition, and is only slightly attacked by acids. Fused with potassium and sodium hydroxide both modifications yield borates.

Boron Hydride, probably BH_3, is only known mixed with hydrogen. It results when hydrochloric acid acts upon magnesium boride. A solid boron hydride is produced on heating boron trioxide with sodium, or borax with magnesium powder. It has not been obtained pure.

Boron Trichloride, BCl_3, may be prepared by heating boron in chlorine, or conducting a stream of the latter over an ignited mixture of the trioxide and carbon (see Silicon and Aluminium Chlorides):

$$B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 3CO.$$

It is a colorless liquid, of specific gravity 1.35, and boiling at 17°. Its vapor density corresponds to the molecular formula BCl_3. The liquid fumes strongly in the air and is decomposed by water into boric and hydrochloric acids:

$$BCl_3 + 3H_2O = B(OH)_3 + 3HCl.$$

The trichloride also results from the action of the pentachloride of phosphorus upon boron trioxide:

$$B_2O_3 + 3PCl_5 = 2BCl_3 + 3POCl_3.$$

Boron Fluoride, BFl_3, is similar to silicon fluoride, and is produced according to the same methods, by the action of hydrofluoric acid upon the trioxide, or by warming a mixture of the trioxide and calcium fluoride with sulphuric acid:

$$B_2O_3 + 3CaFl_2 + 3H_2SO_4 = 3CaSO_4 + 3H_2O + 2BFl_3.$$

It is a colorless gas, fuming strongly in the air, of specific gravity 66 ($O_2 = 32$), and may be condensed to a liquid under strong pressure. It dissolves very readily in water (700 volumes in 1 volume), producing **Hydrogen Borofluoride,** BFl_4H ($= BFl_3.HFl$), which remains in solution:

$$4BFl_3 + 3H_2O = 3HBFl_4 + H_3BO_3.$$

The reaction is analogous to the formation of hydrofluosilicic acid from silicon fluoride (see p. 163). Hydrogen borofluoride is a monobasic acid, only known in its solution and in its salts.

Boric Acid, $H_3BO_3 = B(OH)_3$, occurs free in nature and in salts. In some volcanic districts, especially in Tuscany, the steam escaping from the earth (fumeroles, etc.) contains small quantities of it. These vapors condense in small natural pools, or are conducted into walled basins. By concentration of the aqueous solution, boric acid separates. To prepare pure boric acid, precipitate a hot solution of borax with nitric acid. The acid separates in colorless, shining scales; it dissolves in 25 parts of water at 14°, or in 3 parts at 100°. The solution shows a feeble acid reaction with litmus; turmeric paper, moistened with it, is colored red-brown after drying. On boiling the solution, boric acid escapes with the steam. An alcoholic solution of the acid burns with a green flame. These reactions afford a ready means for its detection.

When heated to 100°, the acid loses one molecule of water, and passes into the anhydro- or meta-acid, HBO_2, which at 140° is converted into tetraboric acid, $H_2B_4O_7$. When ignited, boric anhydride or *Boron trioxide*, B_2O_3, is produced. This is a fusible, glassy mass, of specific gravity 1.8, and is slightly volatile at a very high heat. Water dissolves the anhydride to boric acid.

It is a very weak acid; and can be expelled from its salts by most other acids. By fusion it removes most acids from their salts, in consequence of the difficult volatility of its anhydride.

Salts of normal boric acid, $B(OH)_3$, are not known, while the ethers,

$B(O.CH_3)_3$, are. The salts of metaboric acid, $BO.OK$, can be obtained crystallized, but they are very unstable. They are decomposed by carbon dioxide with production of salts of tetraboric acid:

$$4NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3.$$

The latter, from which the ordinary borates are derived (see Borax), may be viewed as an anhydro-acid, produced by the union of four molecules of trihydric boric acid (compare p. 238):

$$4B(OH)_3 - 5H_2O = H_2B_4O_7.$$

On heating amorphous boron in a stream of nitrogen or ammonia, or by igniting a mixture of the trioxide and carbon in nitrogen gas, there is formed *Boron nitride*, BN. This is a white amorphous powder, which gives forth an extremely intense greenish-white light when heated in a gas flame. Boric acid and ammonia result when steam at 200° is conducted over the nitride:

$$BN + 3H_2O = B(OH)_3 + NH_3.$$

In the heat of the electric furnace carbon unites with boron to *Boron carbide*, B_6C, which is very similar to carborundum, but is harder than the latter. It consists of black, brilliant crystals, of specific gravity 2.5. It is exceedingly stable (Moissan).

PERIODIC SYSTEM OF THE ELEMENTS.

In the preceding pages we have studied the non metals and their compounds with hydrogen, the halogens and oxygen. In their entire behavior they arrange themselves in four natural groups, the members of which show unmistakable family similarities. It is only in the case of boron and of hydrogen and the new constituents of air that allied members have not been found. Attention has been repeatedly called to the gradation in the similarity of the group members, which seems to increase with the rise of the atomic weight, and also to the relations of the various groups to one another—relations observed among the metals. All these points appear more striking and more regularly, if the elements be considered in the arrangement which the periodic system assigns them.

From the time the first atomic weight determinations were made, regularities between the atomic weights and the properties of the elements were thought to exist. One of the first chemists to surmise this was J. W. Döbereiner, whose views were clear and definite in contrast to the fantastic, mathematical sophistries of many of his successors, especially those of the Frenchman Chancourtois, who recently has been unjustly heralded as the forerunner of D. Mendelejeff and Lothar Meyer, the founders of the periodic system.*

---

* See Döbereiner, Pogg. Ann. 15 (1829), 301; Lothar Meyer, Ann. Chem. Suppl. 7 (1871), 354; Mendelejeff, *ibid.*, Suppl. 8 (1872), 133; reprinted in Nos. 66 and 68 of Ostwald's Klassiker der exakten Wissenschaften. For the history of the system see Mendelejeff, Principles of Chemistry (1891), 683, 692; L. Meyer, Modern Theories of Chemistry (1883); also K. Seubert, Z. f. anorg. Chem. 9 (1895), 334.

Arranging the elements according to increasing atomic weight we observe that similar elements return after definite intervals. Thus they arrange themselves in several periods:

1.	Li	Be	B	C	N	O	Fl										
2.	Na	Mg	Al	Si	P	S	Cl										
3.	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Ga	Ge	As	Se	Br
4.	Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
5.	Cs	Ba	La	(Ce	Nd	Pr)	—	—	—	—	—	—	—	—	—	—	—
6.	—	—	Yb	—	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—
7.	—	—	—	Th	—	U	—	—	—	—	—	—	—	—	—	—	—

Hydrogen has no family: it alone would form the first period, and is therefore omitted, as are also helium, argon, and the other recently discovered constituents of the air, because their chemical nature is not known; the positions of tellurium and iodine have also been exchanged, on the presumption that the atomic weight assigned tellurium at present is too high.

The *period system*, or the *law of periodicity*, which is indicated by this arrangement, declares that the *properties of the elements are periodic functions of their atomic weights.*

The first two series, lithium (Li) to fluorine (Fl), and sodium (Na) to chlorine (Cl), present two periods of seven members each, in which the corresponding (above and below) members exhibit a great but not complete analogy. Sodium resembles lithium; magnesium, beryllium; chlorine, fluorine, etc. Then follow two periods, consisting of seventeen elements each: potassium (K) to bromine (Br), and rubidium (Rb) to iodine (I). The series 5 and 6 are incomplete, and together probably constitute a period. In the seventh series there are as yet but two elements: thorium = 232 and uranium = 239.5. Thus result three *great periods*, whose corresponding members exhibit an almost complete analogy: the elements K, Rb, Cs; Ca, Sr, Ba; Ga, In, Tl; As, Sb, Bi, etc., are so similar that they remind us of the homologous series of the carbon compounds (compare p. 153), and, therefore, can be designated as *homologous* elements. It is only in the third great period (series 5 and 6) that the middle members exhibit any variations.

Now on comparing the three great periods with the two small ones, we discover that the first members are analogous to each other; K, Rb, Cs, resemble Na and Li; Ca, Sr, Ba, resemble Mg and Be. Then the similarity gradually lessens, disappears apparently in the middle members, and only appears again toward the end of the periods: I and Br resemble chlorine and fluorine; Te and Se, sulphur and oxygen; Bi, Sb, As, phosphorus and nitrogen, etc. The character or the function of the three great periods is therefore other than that of the two small periods. But in all five periods we can detect a gradual, regular alteration in the properties of the adjoining *heterologous* elements. This is particularly manifest in the measurable physical properties, all of which show a maximum or minimum in the middle of the periods (of both the great and the small).

The same regularity exhibits itself even in chemical properties, in the two small periods, especially in the valence of the elements in their compounds with hydrogen or the hydrocarbon groups CH_3, C_2H_5, etc. (designated by R; compare p. 247). The hydrogen valence rises and falls periodically with the specific gravity:

I	II	III	IV	III	II	I
NaR	MgR_2	AlR_3	SiH_4	PH_3	SH_2	ClH.

On the other hand, the maximum valence of the elements with reference to oxygen increases gradually if chlorine be regarded as septivalent in perchloric acid (pp. 171, 173):

I	II	III	IV	V	VI	VII
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	(Cl_2O_7).

The chemical valence expresses itself somewhat differently in the three great periods. In them we have a *double periodicity;* thus, *e. g.*, with the salt-forming oxides: *

I	II	III	IV	V	VI	VII
K_2O	CaO	Sc_2O_3	TiO_2	V_2O_5	CrO_3	Mn_2O_7

II	II	III	IV	V	VI	VII
CuO	ZnO	Ga_2O_3	GeO_2	As_2O_5	(SeO_3)	(Br_2O_7).

In consequence of this double periodicity, the first seven and the last seven members of the two great periods, with respect to their valence (and consequently also their compounds), resemble the seven members of the two small periods. To bring out this double periodicity and analogy, the first seven and last seven members of the great periods are divided into two series, and arranged under the corresponding seven members of the small periods.

In this way the three middle members of the great periods (which are found between the dotted lines of the table, p. 244) come to stand apart, as they have no analogues. In this manner arises the following table, in which the seven (or ten) vertical columns include homologous elements:

Li	Be	B	C	N	O	Fl	
Na	Mg	Al	Si	P	S	Cl	
K	Ca	Sc	Ti	V	Cr	Mn	Fe Ni CO
Cu	Zn	Ga	Ge	As	Se	Br	
Rb	Sr	Y	Zr	Nb	Mo	—	Ru Rh Pd
Ag	Cd	In	Sn	Sb	Te	I	
Cs	Ba	La	Ce	(Nd,Pr)	—	—	
—	—	Yb	—	Ta	W	—	Os Ir Pt
Au	Hg	Tl	Bi	Pb	—	—	

In the table (on p. 246) we have presented the same grouping of the elements, together with their atomic weights, given in round numbers.

When the periodic grouping of the elements was first presented, the atomic weight of indium and that of uranium had to be doubled, if they were to occupy the places indi-

---

* The elements are given here with their highest oxygen valence. Perbromic anhydride, Br_2O_7, and selenic anhydride, SeO_3, have not been prepared, although some of their derivatives are known. Iron, cobalt and nickel have been omitted because their highest oxides are not well defined.

The Periodic System of the Elements.

		I Group.	II Group.	III Group.	IV Group.	V Group.	VI Group.	VII Group.	VIII Group.		
H-Compounds. Highest salt-forming oxides.		— M_2O	— MO	— M_2O_3	MH_4 MO_2	MH_3 M_2O_5	MH_2 MO_3	MH M_2O_7	MO_3	MO_2	MO (M_2H)
Periods.	Series.										
I	1st	Li 7	Be 9	B 11	C 12	N 14	O 16	Fl 19			
II	2d	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.4			
III	3d	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Ni 59	Co 59
	4th	Cu 63	Zn 65	Ga 70	Ge 72	As 75	Se 79	Br 80			
IV	5th	Rb 85	Sr 87	Y 89	Zr 90	Nb 94	Mo 96	— 100	Ru 102	Rh 103	Pd 106
	6th	Ag 108	Cd 112	In 114	Sn 118	Sb 120	(?)Te 127	I 126 5			
V	7th	Cs 133	Ba 137	La 138	Ce 140	(Pr 140, Nd 144)	—	Sa 150	—	—	—
	8th	—	—	—	—	—	—	—			
	9th	—	—	Yb 173	—	Ta 183	W 184	—	Os 191	Ir 193	Pt 195
	10th	Au 197	Hg 200	Tl 204	Pb 207	Bi 208	—	—			
		—	—	—	Th 232	—	U 239	—			

cated for them by the system. All such alterations have been confirmed by recent investigations. The series of gold, iridium, platinum and osmium did not accord with the system, which rather demanded the following: Osmium, iridium, platinum and gold. This requirement was satisfied by a redetermination of the atomic weights of these elements by Seubert [Ann. Chem. (1891) 261, 272]. Hence, the periodic system offers a control for the numbers of the atomic weight, while formerly they appeared to be irregular, and, at the same time, accidental. We are consequently justified, until we have more evidence to the contrary, in assuming that the determinations of the atomic weight of tellurium have placed that value too high. If it should finally be proved to be greater than that of iodine, then the periodic system would be seriously affected in its foundation; it would then lose its claim to being a natural law—for this would not tolerate an exception.

Mendelejeff, on the basis of the periodic system, predicted in a manner similar to that shown by Leverrier in his precalculation of neptune, the existence of new, not yet known, elements which correspond to unoccupied, free places or gaps in the table. In fact, three such gaps have been filled by the discovery of gallium, scandium, and germanium; their properties have shown themselves to be perfectly accordant with those deduced from the periodic system. [It may be stated here that Döbereiner, on the basis of the law of Triads,—Cl, Br, I; Li, Na, K; Ca, Sr, Ba, etc.: $\frac{Cl + I}{2} = Br$, etc.,—predicted two elements, which should form a triad with fluorine, and one a complete series with phosphorus and arsenic, but the prediction has not been realized.] At present, only the first homologue of manganese (with atomic weight of about 100) is wanting. In the very incomplete series of period V, it is probable that the poorly investigated elements mentioned on p. 27 will find place (see p. 244).

The entire character of a given element is determined to a very high degree by the law of periodicity; hence, all physical and chemical properties of the same are influenced by its position in the system. These relations we will examine more closely in the individual groups of the metals, and here confine ourselves to a notice of some general relations, and the connection of atomic weight with the chemical valence of the elements.

The relation of metalloids to metals is shown with great clearness in the periodic system. The first members of all periods (on the left side) consist of electro-positive metals, forming the strongest bases, the alkalies—Cs, Rb, K, Na, Li, and metals of the alkaline earths—Ba, Sr, Ca, Mg, and Be. The basic character diminishes successively, in the following heterologous members, and gradually passes over into the electro-negative, acid-forming character of the metalloids Fl, Cl, Br, I. Here is observed that, in the periods following each other, with higher atomic weights, the basic metallic character constantly exceeds the metalloidal. The first period comprises five metalloids (B, C, N, O, Fl), the second only four (Si, P, S, Cl), the fourth and fifth periods each only three (or two) metalloids (As, Se, Br, and Sb, Te, I), which, at the same time, become less negative. With the metalloidal nature is combined the power of forming *volatile* hydrogen compounds. Similar volatile derivatives are also afforded by the metalloids with the univalent hydrocarbon groups (as CH_3, C_2H_5, C_3H_7, etc.), which resemble hydrogen in many respects. Such metallo-organic compounds, in which the elements show the same valence as in the hydrogen compounds, are also produced by the metals adjacent to the metalloids:

$$\overset{II}{Mg}(CH_3)_2 \quad \overset{III}{Al}(CH_3)_3 \quad \overset{IV}{Si}(CH_3)_4 \quad \overset{III}{P}(CH_3)_3 \quad \overset{II}{S}(CH_3)_2 \quad \overset{I}{Cl}CH_3.$$

Their stability gradually diminishes with the increasing basic nature of the metals; hence, in the three large periods, this power extends only to Zn, Cd, and Hg.

In consequence of the opposite character of the two ends of the periods, there are in the table representing the double periodicity of the great periods (pp. 244 and 246) two sub-groups each, with the seven vertical groups; on the left with the more positive, basic, and on the right with the more negative, metalloidal elements. Thus in group VI, in addition to O and S (belonging to the small periods) stands the more basic sub-group Cr, Mo, W, and the metalloids Se and Te; in group II stand the strong basic metals Ca, Sr, Ba, and the less basic heavy metals Zn, Cd, Hg. The elements of group VIII form the gradual transition from the latter to the former.

Periodicity of Chemical Valence.—Group I of the table comprises the univalent metals, group II the bivalent. In group III are the trivalent metalloid, boron, and the trivalent metals Al, Sc, Y, and Ga, In, Tl. In the quadrivalent carbon group the valence arrives at its maximum; from here it gradually decreases with increasing atomic weight; the nitrogen group is trivalent, the oxygen group is bivalent, that of the halogens univalent. This valence is derived from the compounds with hydrogen and hydrocarbons (compare p. 247), or where such do not exist, as in the case of boron and many metals, from the halogen compounds:

			IV	III	II	I
			CH_4	NH_3	OH_2	FlH
I	II	III	IV	III	II	I
$LiCl$	$BeCl_2$	BCl_3	CCl_4	NCl_3	OCl_2	Fl_2
$NaCl$	$MgCl_2$	$AlCl_3$	$SiCl_4$	PCl_3	SCl_2	Cl_2.

The elements of the first four groups are not capable of yielding higher compounds with the halogens.* On the other hand, as we have seen, the higher analogues of nitrogen and other metalloids can unite with a larger number of halogen atoms (see pp. 169, 170). The higher valence of these elements is more manifest in the more stable oxygen compounds. On bringing together the *highest oxides* of the seven groups capable of forming salts (salt-building oxides), we get this series:

I	II	III	IV	V	VI	VII
Li_2O	BeO	B_2O_3	CO_2	N_2O_5	SO_3	(I_2O_7).

The elements of the first four groups in their oxygen compounds exhibit, consequently, the same valence as in the compounds with hydrogen (or hydrocarbon radicals) and the halogens; in the last three series, however, there is noticed a constant increase of valence for oxygen.†

---

* Recently halide derivatives of cæsium and rubidium of the formulas CsM_3 and CsM_5 have been prepared (see Cæsium).

† The compound S_2O_7, sulphur heptoxide (p. 188), evidently does not fit in here. It very probably belongs to the true peroxides with the chain –O–O–, so that its composition does not give a definite answer as to the valence of sulphur.

Besides these highest oxides, remarkable for their greater stability, the elements of the last three groups afford lower oxides, returning in this manner to the hydrogen valence:

$$\begin{array}{ccc} \overset{\mathrm{III}}{\mathrm{P_2O_3}} & \overset{\mathrm{IV}}{\mathrm{SO_2}} & \overset{\mathrm{V}}{\mathrm{I_2O_5}} \\ & \overset{\mathrm{II}}{\mathrm{SCl_2}} & \overset{\mathrm{III}}{\mathrm{(Cl_2O_3)}} \\ & & \overset{\mathrm{I}}{\mathrm{Cl_2O}} \\ \hline \mathrm{PH_3} & \mathrm{SH_2} & \mathrm{ClH.} \end{array}$$

The hydroxyl compounds of the elements of the seven groups are analogous to the oxides in constitution. They afford the following series, expressing the maximum valence (compare p. 169):

$$\overset{\mathrm{I}}{\mathrm{Na(OH)}} \quad \overset{\mathrm{II}}{\mathrm{Mg(OH)_2}} \quad \overset{\mathrm{III}}{\mathrm{Al(OH)_3}} \quad \overset{\mathrm{IV}}{\mathrm{Si(OH)_4}} \quad \overset{\mathrm{V}}{\mathrm{P(OH)_5}} \quad \overset{\mathrm{VI}}{\mathrm{S(OH)_6}} \quad \overset{\mathrm{VII}}{\mathrm{Cl(OH)_7}}.$$

The hydroxyl compounds of the elements of the first four groups exist in free condition, excepting that of carbon, $C(OH)_4$, which is only represented in its derivatives. The strong basic character of the hydroxides of group I (NaOH) diminishes, step by step, in the succeeding groups, down to the weak acid hydrate, $Si(OH)_4$. The hydrates of the last three groups are of acid nature, and mostly unstable or not known. By the elimination of one, two and three molecules of water they yield the ordinary acids:

$$\begin{array}{ccc} \overset{\mathrm{V}}{\mathrm{PO(OH)_3}} & \overset{\mathrm{VI}}{\mathrm{SO_2(OH)_2}} & \overset{\mathrm{VII}}{\mathrm{ClO_3(OH)}}. \\ \text{Phosphoric acid.} & \text{Sulphuric acid.} & \text{Perchloric acid.} \end{array}$$

The non-saturated hydroxides behave in the same way:

$$\begin{array}{ccc} \overset{\mathrm{III}}{\mathrm{P(OH)_3}} & \overset{\mathrm{IV}}{\mathrm{S(OH)_4}} & \overset{\mathrm{V}}{\mathrm{Cl(OH)_5}} \\ & .\;. & \overset{\mathrm{III}}{\mathrm{Cl(OH)_3}} \\ & .\;. & \overset{\mathrm{I}}{\mathrm{Cl(OH)}}. \end{array}$$

Sulphurous acid, $SO(OH)_2$, is derived from the hydrate, $S(OH)_4$; chloric acid, $ClO_2.OH$, from the hydrate, $Cl(OH)_5$; and chlorous acid, $ClO.OH$, from the hydrate, $Cl(OH)_3$. The hydrates, $P(OH)_3$ and ClOH, are very unstable, and the first appears to pass readily into $HPO(OH)_2$ (compare p. 215).

It has been already shown in the case of periodic, sulphuric, and nitric acids, how the so-called hydrates with water of crystallization (regarded as molecular compounds) are explained by the acceptance of the existence of such hydroxyl derivatives. The same may be done for many salts with water of crystallization.

Thus, we see, and in the following pages will find it more extensively developed, that the relations of valence of the elements have their complete expression in the periodic system, are regulated by it, and hence we must conclude that, in fact, the valence is not only a property attaching to the elements *per se*, but is influenced also by the nature of the combining elements; the hydrogen valence is constant, the valence of oxygen and the halogens, on the contrary, varies according to definite rules. Valence, therefore, is a relative function of the elements (p. 169).

The periodic system, the natural division of the elements, apparently emphasizes the fact that the atoms of the chemical elements are aggregations or condensations of one and the same primordial substance—the unity of matter, which corresponds to the unity of force already known to us. It is only by assuming a primordial substance that the periodic dependence of the properties of the chemical elements upon the magnitude of the atomic weights can be comprehended.

It was suggested that hydrogen was this original substance, because it appeared as if all atomic weights had to be expressed in whole numbers—that is, multiples of the atomic weight of hydrogen, taken as unit (Prout 1815, Meinecke 1818). More accurate determinations, made with exceeding care by Stas, demonstrated this not to be true in all cases [J. S. Stas, Untersuchungen über die Gesetze der chemischen Proportionen, über die Atomgewichte und ihre gegenseitigen Verhältnisse, Deutsch von Aronstein, Leipzig, 1867]. The inquiry was then made as to whether the variations of the atomic weights from whole numbers could not be occasioned by definite amounts of ponderable ether entering or escaping in the chemical transposition of bodies. The experiments of H. Landolt on this point gave a negative reply, thus cutting off the last avenue which remained open to the hypothesis of Prout and Meinecke [Ber. **26** (1893), II, 1820].

It must be borne in mind, however, that it is not only the atomic weight which influences the properties of an element, but that the molecular weight and the energy of the molecule exercise great influence in this direction. The occurrence of allotropic modifications of an element can only be explained on this assumption. These, in their general deportment, often differ more from one another than two different but related elements. Phosphorus in its varieties is a most striking example. Similar relations have been noticed with carbon—soot, graphite, diamond, and with oxygen—ordinary oxygen and ozone. It is only the power of uniting a definite number of different atoms which remains in all varieties of one element. Thus, red phosphorus on oxidation yields the same oxides and acids as the yellow, and by burning the diamond the same carbonic acid is produced as with soot and graphite. The valence which one element shows with reference to other elements, is, therefore, primarily a function of the atomic weight. Its physical properties, on the other hand, are *also* dependent upon the molecular weight and the energy of the molecule.

The law underlying the periodic system will only be recognized perfectly and in its entirety when it becomes possible to deduce the properties of the different varieties of an element from the atomic weight of the latter.

Again, these allotropic modifications indicate that bodies can be formed by a different arrangement of similar atoms, and it is only by keen scientific observation that varieties of one and the same substance can be detected. The elements could similarly consist of varieties or allotropic forms of some one primordial form of matter.

THE METALS.

Although there is no sharp line of demarcation between metals and non-metals, yet these two classes of bodies are characteristically distinctive in their entire deportment, as may be plainly seen in the periodic system of elements. In physical respects the character of metals is determined by their external appearance and by their ability to conduct heat and electricity; chemically, it shows itself chiefly in the basicity of the oxygen compounds; yet we see that with the increase of the number of the oxygen atoms, the basic character gradually diminishes and becomes acidic. Gaseous compounds of the metals with hydrogen are not known.

PHYSICAL PROPERTIES OF THE METALS.

At ordinary temperatures all the metals excepting mercury are solid, slightly volatile bodies. They are opaque, and only a few, like gold, permit the passage of light to a limited extent when beaten into thin leaflets. In compact mass they exhibit metallic luster and mostly possess a whitish-gray color; gold and copper are, however, brilliantly colored. In powder form almost all the metals are black.

Most of them crystallize in the forms of the regular system; only a few, showing a metalloidal character, are not regular. Thus antimony and bismuth crystallize in the hexagonal system, and tin is quadratic.

The specific gravities of the metals vary greatly, from 0.59 to 22.5, as seen from the following arrangement:

Lithium,	0.59	Germanium,	5.47	Lead,	11.37
Potassium,	0.87	Zinc,	7.1	Palladium,	11.5
Sodium,	0.97	Tin,	7.3	Thallium,	11.8
Rubidium,	1.52	Iron,	7.8	Mercury,	13.55 *
Calcium,	1.57	Cobalt,	8.5	Gold,	19.3
Magnesium,	1.74	Copper,	8.9	Platinum,	21.5
Aluminium,	2.6	Bismuth,	9.8	Iridium,	22.4
Barium,	3.75	Silver,	10.5	Osmium,	22.5

In general the specific gravities of the metals, and also those of the metalloids, increase with the atomic weights; they stand more especially in sharp periodic dependence with reference to the latter. The first members of all periods possess low specific gravities; the latter grow

---

* Liquid; solid = 14.2.

gradually until the middle of the period, when the maximum is attained, and then they again decrease (p. 245). These relations show themselves more fully if, instead of the specific gravity, we compare the specific volumes or atomic volumes; *i. e.*, the quotients from the atomic weights (A) and specific gravities (d):

$$\frac{A}{d} = \text{specific volume.}$$

These quotients express the relative value of the atoms (in solid or liquid state). Thus the atomic volume of lithium $\left(\frac{7.03}{0.59}\right) = 11.9$, that of potassium $\left(\frac{39.15}{0.87}\right) = 45.0$; *i. e.*, the potassium atom occupies a space 3.8 times larger than that of the lithium atom. The periodic alterations of the atomic values are in opposition to those of the specific gravities, as the former are obtained by the division of the atomic weights by the specific gravities. Therefore, the atomic volumes decrease gradually, commencing with the first members of the periods, attain a minimum in the middle of the periods, and then increase again up to the last members. On the other hand, we find that with the homologous elements (the vertical series) an increase in the atomic volumes almost invariably occurs as the atomic weights increase.

The metals whose specific gravities are less than 5 are termed *light metals*, the rest *heavy metals*. The naturally occurring compounds of the heavy metals are termed *ores*.

Most metals are very *malleable* and *tenacious*, hence can be beaten into thin plates and leaves, and drawn out into wires; gold and silver are the most malleable. A few, like bismuth and tin, possess a metalloidal character, are *brittle*, and may be pulverized like antimony and arsenic.

Heat will fuse all metals, although some require high temperatures. The fusing points of the most important of them are the following:

Mercury,	—39°	Aluminium,	650°
Rubidium,	+38°	Germanium,	900°
Potassium,	62°	Silver,	960°
Sodium,	96°	Gold,	1060°
Tin,	230°	Copper,	1090°
Bismuth,	265°	Cast iron,	1150°
Cadmium,	320°	Wrought iron,	1600°
Lead,	330°	Platinum,	1775°
Zinc,	420°	Iridium,	1950°

Ruthenium, osmium and also chromium, molybdenum, uranium, tungsten and vanadium melt with greater difficulty than platinum.

A greater volatility also corresponds to the greater fusibility. Mercury boils at 357°; potassium and sodium at about 700°; cadmium at 770°; zinc about 950°, and the difficultly fusible metals may be also volatilized in the electric furnace.

Metallic borides, silicides and carbides (p. 163) withstand temperatures which volatilize platinum, calcium and carbon (Moissan).

All these physical properties bear a periodic dependence to the atomic weights, as will be more plainly indicated in the indvidual groups.

Until lately the highest temperature attainable for scientific and technical uses was about 2000°. The idea of using the electric arc to extend the range of temperature is not new, but the actual achievement was first accomplished by the French chemist, H. Moissan, by the construction of the electric furnace. The principle involved in the latter is to expose a substance to the heat of the electric arc in a space as small as possible and surrounded by fire-resisting material. The action is then due to heat and not to electricity. Moissan in this way obtained a temperature of 3500° C. The furnace model first used by him in 1892 is sketched in Fig. 68. It consists of two blocks of unslaked lime. The lower contains a groove for the carbon electrodes *E*, *E*, and about the middle is a depression in which the material is placed and upon which the heat of the arc is to act. The material can also be exposed in a small carbon crucible. The upper portion is slightly arched above the arc. As the lime soon melts on the surface and becomes soft the arch acts as a heat reflector. For the various forms of electric furnaces consult H. Moissan, Der elekt. Ofen, 1897; also Liebetanz, Calciumkarbid- und Acetylentechnik, pp. 38–79. Compare Z. f. anorg. Ch. 22 (1896), 293.

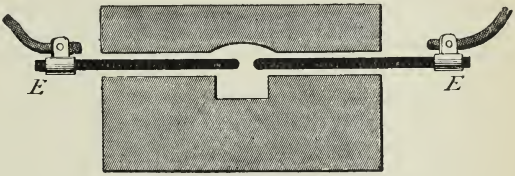


FIG. 68.

SPECIFIC HEAT. ATOMIC HEAT.

Of all physical properties of the elements, from a chemical standpoint, their heat capacity is the most important, as it can serve for the determination of the atomic weights. The *specific heat* of a substance is the quantity of heat which increases its mass unit 1° in temperature. Heat quantities are measured in either large or small calories (p. 66), and according as one or the other is chosen, the expression for the mass unit will be 1 kilogram or 1 gram. As water, of all substances, possesses the greatest specific heat, and as this also serves as unit; therefore, for all other bodies the specific heat represents the fraction of a calorie which raises their mass unit 1°.

The atomic heat of an element is the product of its specific heat (H) and atomic weight (A). Dulong and Petit (1818) discovered the remarkable fact that *the solid elements possess approximately the same atomic heat.* It is about 6.4:

$$A\,.\,H = 6.4.$$

For silver $A = 107.93$ and $H = 0.057$; $A\,.\,H = 6.1$; for lead $A = 206.9$, $H = 0.031$, $A\,.\,H = 6\ 4$; for potassium $A = 39.15$, $H = 0.166$, $A\,.\,H = 6.5$—*i. e.*, 107.93 grams of silver, 206.9 grams of lead, and 39.15 grams of potassium are heated by approximately 6.4 small calories through 1° of temperature, or 107.93, 206.9 and 39.15 kilograms are raised 1° by 6.5 large calories. The equation $A\,.\,H = 6.4$ also indicates that the specific heats of two elements are to each other approximately as their atomic weights—the greater the atomic weight, the smaller the specific heat.

It is only in the case of a few of the elements that the atomic heat varies widely from the mean 6.4, *e. g.*, sulphur is 5.7, phosphorus 5.9, silicon 4.6, germanium 5.6, while carbon is 2–2.8, boron 2.6 and beryllium 3.7. These elements have low atomic weight and are either metalloids or resemble metalloids.

These variations from the mean are in part explained by the change in specific heat with the temperature. It was known before that these show a slight increase with the temperature, but it is only recently (1875) that H. F. Weber has proved that the increase is very considerable for the elements C, B and Si, which, at medium temperatures, possess a remarkably low atomic heat; that, beyond a definite temperature, the atomic heat becomes tolerably constant, and then almost agrees with the law of Dulong and Petit. According to Nilson, beryllium shows a similar deportment:

	H	A	H × A
Diamond, graphite, above 900°, ...	0.459	12.00	5.5
Boron, above 600°, ...	0.5	11	5.5
Silicon, above 200°, ...	0.204	28.4	5.8
Beryllium, above 257°, ...	0.58	9.1	5.3

From this close agreement of the found atomic heat of the metals with the mean, it follows, without doubt, that there does occur a regularity, and we must conclude that the slight variations, apart from the inaccuracy of the observations and the impurities of the substances used, are influenced by physical causes of an unknown nature. Hence, the specific heat may serve for the derivation of the atomic weight of the elements; *the atomic weight is equal to the constant* 6.4 *divided by the found specific heat:*

$$A = \frac{6.4}{H}.$$

The atomic weights derived from the specific heat—the so-called *thermal atomic weights*—agree in almost all instances with those obtained from the vapor density of the free elements or their volatile compounds. Where no volatile compounds of an element are known, the specific heat is the only certain means of fixing the actual atomic weight. The equivalent weight, 38 ($\overset{I}{In}Cl$), of indium was fixed with great accuracy by analysis; it was, however, unknown whether the atomic weight was double or triple that quantity. The specific heat of indium was found to be 0.0569, from which the atomic weight would be $\frac{6.4}{0.0569} = 112$, a number closely approaching the trebled equivalent weight of indium, 114 (= 38 × 3). From this it follows that the true atomic weight of indium is 114 and that indium is trivalent ($InCl_3$).

In their solid compounds the elements retain the specific heat; hence the molecular heat is nearly equal to the sum of the atomic heats of the elements constituting the molecules—law of F. Neumann and H. Kopp. Hence the atomic heat of elements not known in solid condition may be derived from the molecular heat of their compounds. In this manner the following atomic heats are found: For nitrogen, 5.0; for chlorine, 6; for oxygen, 4; for fluorine, 5; for hydrogen, 2.3; for carbon, 1.8.

In the free state the gaseous elements usually have a slighter atomic heat, as seen from the following table:

	A	H*	A × H
Oxygen,	16	0.156	2.5
Hydrogen,	1.01	2.405	2.4
Nitrogen,	14.04	0.172	2.4
Chlorine,	35.45	0.093	3.3

ISOMORPHISM.

As indicated in the preceding pages, the atomic weights of the elements may be derived directly from the specific heat of solids, while from the gas density of the volatile compounds we get the molecular weights, and from the latter, indirectly, ascertain the atomic weights (compare p. 80). A third, although less general and certain, means of determining the atomic weight is afforded by *isomorphism*. By this is understood the phenomenon observed by Mitscherlich (1819). Characteristics of the isomorphism of two bodies are:

(1) Similarity in crystalline form, whereby the symmetry properties agree perfectly and the geometrical constants nearly coincide (see pp. 31, 38); (2) the power of forming within certain definite limits mixed crystals in any desired quantity by weight without altering the crystal form; (3) the power of overgrowth, *i. e.*, crystals of the one substance being able to continue their growth in supersaturated solutions of the other compound. From Mitscherlich's discovery we can conclude from the isomorphism of two compounds that they are similarly constituted and have an equal number of atoms in the molecule. Accordingly the quantities of the elements, occurring in isomorphous mixtures, would be to each other as their atomic weights, and this would make it possible to establish an incorrect atomic value. For example, the metals calcium, strontium and barium do not afford volatile derivatives. Their atomic weights could not be deduced from their thermal capacity, and it was the isomorphism of many of their compounds with those of magnesium that determined the same; the quantities of these elements, replacing 24.36 parts by weight of magnesium (1 atom), were accepted as the true atomic weights.

In the present state of chemistry we attach but secondary importance to isomorphism as a method of determining atomic weights because it is frequently very difficult to demonstrate that isomorphism is actually present, for the coincidence in geometrical constants requires to be only approximate, the ability to yield mixed crystals occurs in every imaginable degree and bodies possessing not the slightest chemical similarity do show overgrowths. It is indeed true that bodies similar chemically often exhibit like crystalline form, and the power of forming mixed crystals also increases the greater the similarity in chemical properties.

CHEMICAL PROPERTIES OF THE METALS.

Alloys.—Many metals may be so mixed by fusing them together that a solid, homogeneous mass will result upon cooling; the constituents cannot be separated then by mechanical means. Such a mixture is based upon a molecular interpenetration; it cannot be distinguished from a mere mechanical mixture and it bears the name *alloy* (*legere*, put together).

---

* By constant volume.

A great deal of heat is frequently developed just as in a chemical union by fusing metals or by bringing together those already melted. Yet alloys in general cannot be considered chemical compounds; their composition, even in the case of those which crystallize, is rarely according to the atomic ratio. They should rather be regarded as *solid solutions* of one metal in another or of metallic compounds in a metal, if, following Ostwald, a homogeneous mixture of various substances (showing no variability) is defined, without reference to its state of aggregation, as a *solution.*

Many molten metals may be mixed just like water and alcohol in every proportion with one another, *e. g.*, tin and lead; others in a less degree, similarly to ether and water, *e. g.*, zinc and lead. The second class of alloys occurs more frequently. Usually metals which are similar chemically alloy more readily with one another than those which exhibit marked differences in their chemical behavior.

Many alloys can be obtained crystallized, yet in actual practice crystallization is avoided because it diminishes the solidity, ductility, etc.

As a rule, the density of an alloy cannot be calculated from its constituents, but this is possible with a mere mechanical mixture. Many alloys exhibit a very definite condensation (contraction), *e. g.*, silver-gold, copper-tin; others a distinct expansion: copper-silver, antimony-tin, tin-lead, while others do not manifest either of these properties: copper-gold, antimony-bismuth.

The color of alloys does not correspond to the quantity of their constituents, for copper alloys, with 30 per cent. of tin, are white in color, and pure yellow with the same amount of zinc. The bright color disappears with 60 per cent. of zinc. Aluminium changes the color of copper readily; the same is true of nickel, as may be seen in the coin, containing about 25 per cent. of nickel and 75 per cent. of copper. Gold possesses slight coloring power. Gold and silver alloys having 30 per cent. of gold possess a pure silver-white color.

The melting point of an alloy is generally lower than would be expected from the melting points of its constituents. An alloy of 8 parts of lead, 15 parts of bismuth, 4 parts of tin, and 3 parts of cadmium melts at 68°, although each of these metals melts above 200°. Potassium (m. p. 62°) and sodium (m. p. 96°) unite in the ratio of their atomic weights to an alloy which is liquid, like mercury, at the ordinary temperature.

Quite frequently molten alloys manifest the tendency on slow cooling to separate into several compounds which differ in composition, fusibility, etc., from one another. Under these conditions pure metals also separate from many alloys. This process, very important for the preparation of metals, is designated segregation (see Silver).

Alloys often resist acids much better than single metals; however, they frequently dissolve in acids even when the one constituent is insoluble in them. Thus an alloy of 56.5 per cent. of copper and 43.5 per cent. of zinc is scarcely attacked by nitric acid, and in gold-silver alloys, where there is a preponderance of gold, the silver is not dissolved out by nitric acid. If the alloy contains 3 parts of silver to one part of gold the nitric acid will dissolve the silver (quartation).

Mercury is able to dissolve almost all metals, forming alloys known as *amalgams* (from *μάλαγμα*, a soft plaster), which are generally crystallizable. In chemical respects hydrogen is a metal, and very many of the metals combine with it. Palladium, potassium and sodium yield the compounds K_4H_2 and Na_4H_2, which deport themselves as alloys. That antimony yields a gaseous product (SbH_3), is due to its pronounced metalloidal character. The ability of individual metals of the platinum and iron groups to permit the passage of hydrogen at a red heat depends, probably, upon a chemical attraction; hydrogen first dissolves and is then evaporated again.

Metallic Carbides.—These are produced by dissolving carbon in the molten metal or by reducing metallic oxides with carbon. The electric furnace with its high temperatures has been applied in this direction. The researches of Moissan and the technical application of calcium carbide and silicon carbide (carborundum) have given great theoretical and practical importance to the carbides in general (pp. 154, 163). Molten gold, bismuth, lead and tin do not dissolve carbon, and copper and silver very little. The melted platinum metals take it up in large amounts, and upon cooling it separates as graphite. Many other metals, under like conditions, form carbides which crystallize beautifully. Carbides may be arranged in two series:

1. Those decomposed by water at the ordinary temperature. Here belong the carbides of potassium, lithium, Li_2C_2, calcium, barium, strontium ($Me''C_2$), aluminium, Al_4C_3, manganese, MnC, and beryllium.

2. Those which are not affected by water: molybdenum carbide, CMo_2, chromium carbide, Cr_3C_2, etc. The carbides decomposable by water yield hydrogen, methane, acetylene, and also liquid and solid hydrocarbons. Moissan thinks that this behavior affords hints as to the origin of petroleum (see Calcium- and Aluminium Carbide, also p. 252).

Halogen Compounds.—The metals unite directly with the halogens to form compounds, which are not decomposed by water at ordinary temperatures, and, in general, are very stable; on the other hand, the halogen compounds of the metalloids (excepting those of carbon) are easily decomposed by water. These compounds are also produced by the action of the haloid acids upon the free metals, their oxides, hydroxides, and carbonates, whereby they plainly characterize themselves as salts of the haloid acids. A third procedure for the formation of chlorides and bromides, essentially analogous to the first, is based upon the simultaneous action of carbon and chlorine, or bromine upon the oxides (see Aluminium Chloride and Silicon Chloride).

The following types of halogen derivatives exist and show the different valences of the metals:

I	II	III	IV	V	VI
KCl	$ZnCl_2$	$InCl_3$	$SnCl_4$	$TaCl_5$	WCl_6.

OXIDES AND HYDROXIDES—HYDRATES.

The affinity of the metals for oxygen varies. Some of them oxidize in moist air and decompose water, even at ordinary temperatures. Such are the so-called alkalies and alkaline earths (the potassium and calcium groups). Their oxides dissolve readily in water and form strong basic hydroxides or hydrates, KOH, $Ca(OH)_2$, which are usually not decomposed by ignition.

Other metals (the so-called heavy metals) oxidize and decompose water only at higher temperatures; their oxides are insoluble in water, and generally afford no hydroxides, as the latter upon heating readily decompose into oxides (anhydrides) and water:

$$Zn(OH)_2 = ZnO + H_2O.$$

They are of a less basic nature, and their soluble salts usually exhibit acid reaction. Finally, some metals, as gold and platinum (the noble metals), are incapable of combining directly with oxygen. Their oxides, obtained in another way, decompose readily under the influence of heat into metal and oxygen. The universal method for the preparation of insoluble oxides and hydroxides of the heavy metals depends upon the precipitation of the solutions of their salts by alkaline bases:

$$HgCl_2 + 2KOH = 2KCl + HgO + H_2O$$

$$\overset{II}{Cu}SO_4 + 2KOH = K_2SO_4 + \overset{II}{Cu}(OH)_2.$$

The different valences of the metals are most clearly seen in their oxygen derivatives, which form salts. We have the following eight forms or types of the highest salt-producing oxides (see p. 244), corresponding to the eight groups of the periodic system of the elements:

I	II	III	IV	V	VI	VII	VIII
K_2O	MgO	Al_2O_3	SnO_2	Bi_2O_5	CrO_3	Mn_2O_7	OsO_4.

The hydroxides of the first two forms possess a strong basic character and only yield salts with acids. In the hydroxides of the two succeeding forms there is shown an acid-like character together with the predominating basic character. Hence they dissolve in alkalies and form salt-like derivatives with bases, in which hydrogen is replaced by metals, *e. g.*, $Al(ONa)_3$. These higher (normal) hydrates are not very stable, give up water and pass into *meta-hydrates*, which retain the acid character. Thus, from $Al(OH)_3$ is derived $AlO.OH$, which yields salt-like compounds, *e. g.*, $AlO.ONa$; from $Sn(OH)_4$ are derived stannic acid, $SnO(OH)_2$, and its salts, as $SnO(ONa)_2$. The oxides of the next fundamental forms, Bi_2O_5 and Mn_2O_7, are of an acid nature. The corresponding highest hydroxides do not exist; but the salts of the anhydro-acids, derived from them, are known:

$HBiO_3$	H_2CrO_4	$HMnO_4$.
Bismuthic acid.	Chromic acid.	Permanganic acid.

In composition these acids correspond to the following metalloid acids:

HNO_3	H_2SO_4	$HClO_4$.
Nitric acid.	Sulphuric acid.	Perchloric acid.

Salts of osmium tetroxide (OsO_4) are not known.

Like the metalloids, the metals of the last four series form lower oxides and hydrates in which they exhibit a lower valence:

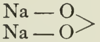
SnO	Bi_2O_3	MnO
$Sn(OH)_2$	$Bi(OH)_3$	$Mn(OH)_2$.

These lower oxides and hydroxides have a basic character, and in their whole deportment resemble the corresponding compounds of the metals of the first three groups.

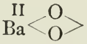
The metals of the first two groups have higher oxygen compounds, called *peroxides*, *e. g.*, Na_2O_2, BaO_2. These do not form corresponding salts. By the action of dilute acids hydrogen peroxide is produced:

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

In consequence of this reaction, it is very probable that in the peroxides, the oxygen atoms are arranged in a chain-like manner as in hydrogen peroxide:



Sodium peroxide.



Barium peroxide.

When concentrated acid acts upon them, oxygen is evolved, and salts of the lower oxides result; heated with hydrochloric acid, chlorine is generated:

$$BaO_2 + 4HCl = BaCl_2 + 2H_2O + Cl_2.$$

Ordinarily, all higher oxides which evolve chlorine with hydrochloric acid are termed peroxides, *e. g.*, PbO_2, lead peroxide, and MnO_2, manganese peroxide. However, these latter compounds do not possess the structure of true peroxides. Lead dioxide, PbO_2, is wholly analogous to tin dioxide, SnO_2, and is capable of combining with bases; it also yields a tetrachloride, $PbCl_4$, which it is true readily breaks down into the dichloride and chlorine; therefore we infer that the two oxygen atoms are in direct union with quadrivalent lead. So manganese is probably quadrivalent in manganese peroxide. The difference between these oxygen compounds and the true peroxides is shown by their inability to form hydrogen peroxide. Persulphuric and percarbonic acids belong to the true peroxides.

Finally, some univalent metals are capable of forming oxides containing four atoms of metal, *e. g.*, K_4O, Ag_4O; these compounds are termed *quadrant oxides* or *suboxides*.

Salts.—By the action of bases upon acids, salts and water result:

$$NaOH + HNO_3 = NaNO_3 + H_2O,$$

whereas oxides and acid anhydrides, *e. g.*, CaO and CO_2, in the absolute absence of water do not combine, or at least only with difficulty.

These salts are also produced like the halides by the action of metals upon the acids:

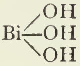
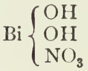
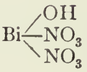
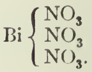
$$H_2SO_4 + Zn = ZnSO_4 + H_2;$$

most of the oxygen acids suffer simultaneous reduction by the hydrogen evolved. This happens with sulphuric acid if it be used in a concentrated form, so that, *e. g.*, in the action of zinc on concentrated sulphuric acid both sulphurous acid and hydrogen sulphide are produced:

$$H_2 + H_2SO_4 = SO_2 + 2H_2O;$$
$$4H_2 + H_2SO_4 = H_2S + 4H_2O.$$

Sulphurous acid, nitric acid and chloric acid are also reduced in dilute solutions (see pp. 184, 186, 203). Phosphoric acid, in contrast to arsenic and antimonic acids, is very stable in the presence of nascent hydrogen (pp. 148, 216). The salts of oxygen acid, like those of the haloid acids, are to be regarded as derived from the acids by replacement of their hydrogen by metals. The acids themselves can be viewed as *hydrogen salts*. This was the conception of H. Davy (1815), of P. L. Dulong (1816), and particularly of J. Liebig (1838), from chemical considerations, and also a little later (1839) of J. Fr. Daniell, from electrolytic reasons.

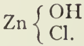
As we have seen, the polybasic acids yield the *primary*, *secondary*, *tertiary*, *etc.*, *salts* by the replacement of one or several hydrogen atoms by metal (see p. 172). In the same manner n-series of salts are derived from n acid bases (which contain n-OH groups):



$Bi\left\{\begin{matrix}OH\\OH\\NO_3\end{matrix}\right.$


$Bi\left\{\begin{matrix}NO_3\\NO_3\\NO_3.\end{matrix}\right.$

Such salts in which not all the hydroxyl groups of the polyacid hydroxide are replaced by acid residues are called *basic*:

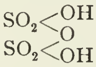
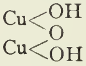
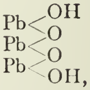

$Pb\left\{\begin{matrix}OH\\NO_3\end{matrix}\right.$

Basic lead nitrate.


$Zn\left\{\begin{matrix}OH\\Cl.\end{matrix}\right.$

Basic zinc chloride.

Besides these basic salts there exist some of another form. We saw that the polybasic acids can combine to form poly- or anhydro-acids; similarly, the *polyhydric* bases form polyhydrates:

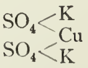




from which basic salts are obtained (see Copper and Lead) by replacement of hydroxides by acid residues.

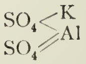
By the replacement of the hydrogen atoms in the polybasic acids or of the hydroxyl groups in the *polyhydric* bases by various radicals we get the so-called *mixed* or *double salts*:


$PO_4\left\{\begin{matrix}K\\NH_4\\H\end{matrix}\right.$

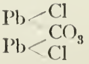
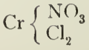
Potassium ammonium phosphate.



Potassium copper sulphate.



Potassium aluminium sulphate.



$Cr\left\{\begin{matrix}NO_3\\Cl_2\end{matrix}\right.$

$MgCl_2 . KCl$ $AuCl_3 . KCl$ $PtCl_4 . 2KCl.$

Just as the fluorides of boron and silicon, $BFl_3 . KFl$, $SiFl_4 . 2KFl$, are derived from peculiarly constituted atomic acids, $HBFl_4$, H_2SiFl_6 (pp. 170, 226), so also many of the so-called double chlorides,* *e. g.*, $PtCl_4 . 2KCl$, must be viewed as atomic in their structure (see p. 271 and under Platinum).

ACTION OF METALS UPON SALTS AND ACIDS.

We have seen that the metals by solution in acids are able to form salts, hydrogen being simultaneously evolved.

The metals deport themselves in the same manner with the salts. Zinc introduced into a solution of copper sulphate is dissolved to sulphate and metallic copper is deposited:

$$Zn + CuSO_4 = ZnSO_4 + Cu.$$

Herein is shown the perfect analogy between acids and salts:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

In chemical nature hydrogen is a metal. Hence the acids may be viewed as hydrogen salts.

The displacement of a metal from its salts by others appears to be influenced by its electrical deportment in so far as it occurs, in general, in accordance with its position in the electric tension series. Indeed the more electro-positive (basic) metals replace the electro-negative (less basic). In the following series each metal throws out from solution those preceding it: Au, Pt, Ag, Hg, Cu, Pb, Sn (Fe, Zn). Iron and zinc precipitate almost all the heavy metals from solutions of their salts. The strongly positive potassium and sodium are able to displace all other metals. This is very evident from their action upon fused haloid salts—a reaction which frequently serves for the separation of the metals in a free condition:

$$AlCl_3 + 3Na = Al + 3NaCl.$$

In its electrical deportment hydrogen stands near zinc; like the latter, it must, therefore, displace all more negative metals. If this does not happen, the cause must be sought in the volatility of hydrogen; in fact, we know that hydrogen, under powerful pressure, is capable of separating gold, silver and some other metals from their salt solutions.

In addition to electrical deportment, the nature of the solution influences the precipitation of one metal by another. Thus, lead separates tin from its chloride, $SnCl_4$, while, on the other hand, tin throws out lead from the solution of its oxide in alkalies. This recalls the fact that iodine is displaced in hydriodic acid and the metallic iodides by chlorine; and that conversely iodine replaces chlorine in its oxygen derivatives (p. 278).

Mylius and Fromm (Ber. **27** (1894) I, 630) claim that when positive metals act upon dilute salt solutions of negative metals, alloys are produced, because in the moment of their precipitation metals are capable of uniting at the ordinary temperature. Generally these alloys are porous, black, and either amorphous or crystalline. The following crystalline compounds were obtained: Cu_2Cd, $AuCd_3$, Cu_3Sn and lead-platinum. Zinc pre-

---

* Consult *American Chemical Journal*, II, p. 291.

cipitates a zinc-silver alloy from dilute silver solutions, which is converted into white crystalline silver by a concentrated silver solution, and also by strong acids:

$$Ag_nZn + 2AgNO_3 = Ag_{(n+2)} + Zn(NO_3)_2.$$

The other alloys are similarly decomposed by acids, the negative element being set free.

ELECTROLYSIS OF SALTS.

Conductors are divided into two classes, depending upon their behavior in the passage of the electric current. *Conductors of the first class* are not decomposed in the passage of the current: the metals, peroxides and carbon. *Conductors of the second class* carry the current with simultaneous decomposition: "Electrolysis"—salts, acids and bases, fused or in aqueous solution. They are also termed electrolytes (p. 92). In most instances the conductivity of the first class diminishes with rise in temperature, while it increases with the second class.

On subjecting a salt in a fused or dissolved condition to the action of an electric current, it is decomposed, so that the metal separates at the negative pole and the acid group or halogen at the positive:

$$NaCl = \overset{+}{Na} + \overset{-}{Cl}$$
$$CuSO_4 = \overset{+}{Cu} + \overset{-}{SO_4}.$$

The liberated acid residues, *e. g.*, SO_4, cannot exist in a free condition; they break down into oxygen and an acid oxide, which, with the water of the solution, again forms the acid:

$$SO_4 + H_2O = H_2SO_4 + O.$$

Thus, in the electrolysis of such salts, the metal and oxygen separate out—the former at the negative, the latter along with free acid at the positive pole (see p. 92 note).

All neutral salts are similarly decomposed. If, however, the metal contained in the salt acts upon water when free, manifestly a secondary reaction must occur at the negative pole. The real electrolytic decomposition of potassium sulphate would then take place according to the following equation:

$$K_2SO_4 = \overset{+}{K_2} + (\overset{-}{SO_4}).$$

The separated potassium decomposes the water with formation of potassium hydroxide and the disengagement of hydrogen:

$$2K + 2H_2O = 2KOH + H_2.$$

Therefore, hydrogen and potassium hydroxide occur as definite decomposition products, at the negative pole (the kathode); at the positive (the anode), however, we have oxygen and sulphuric acid. On coloring the liquid exposed to the electrolysis with a little violet-syrup, that part at the positive pole will become red, owing to the acid formed, while that at the negative pole will be colored green by the base. That the electrolytic decomposition of potassium sulphate and similar salts proceeds in the manner given, may be proved experimentally by using mercury as the negative electrode; then the separated potassium will combine with the mercury and form an amalgam, which will act gradually upon the water.

The bases and acids are decomposed in this manner by the current. Thus, as Davy (1807) showed, molten caustic potash, KOH, breaks down into K and OH; the first separates in metallic form upon the negative pole (and gradually acts upon the fused KOH with the liberation of hydrogen), while at the positive pole water and oxygen appear—produced from the OH-ions:

$$2(OH) = H_2O + O.$$

Acids when electrolyzed behave like hydrogen salts. Hydrochloric acid, for example, breaks down into hydrogen and chlorine. Sulphuric acid (depending upon its strength) is decomposed in aqueous solution into the ions $2H$ and SO_4 or H and HSO_4. The anion SO_4 (or HSO_4) is immediately converted by the water into sulphuric acid and oxygen:

$$2HSO_4 + 2H_2O = H_2SO_4 + O.$$

However, under certain conditions, an appreciable amount of persulphuric acid is produced:

$$2HSO_4 = H_2S_2O_8.$$

[See p. 188 and Richarz, Ber. **21** (1888), 1673.]

The electrolysis of acid sulphates and of acid carbonates can also proceed in the direction last indicated; they break down into kations H and anions $MeSO_4$ and $MeCO_3$, from which arise persulphates and percarbonates: $Me_2S_2O_8$ and $Me_2C_2O_6$; see also p. 231.

In the thirties of the present century Michael Faraday demonstrated that when a compound is decomposed by the electric current the quantity of the material so broken down is proportional to the quantity of electricity which has passed through it. He also discovered the following law bearing his name:

When the electric current passes through different decomposable conductors arranged in series, the quantities of the substances separated simultaneously are to each other as the ratio of their chemical equivalents.

Thus in the simultaneous decomposition of hydrochloric acid, dilute sulphuric acid and ammonia* (pp. 77, 98), equal volumes of hydrogen are liberated, while at the positive pole 1 volume of chlorine, ½ volume of oxygen, and ⅓ volume of nitrogen appear, after the solutions have become saturated with the gases. The quantities decomposed by electrolysis, therefore, bear the following relation:

$$HCl, \frac{H_2SO_4}{2}, \frac{NH_3}{3}.$$

---

* The hydrochloric acid should contain 219 grams in a liter. This can be obtained by mixing 200 grams of fuming hydrochloric acid, of specific gravity 1.185, with 128 grams of water. For the electrolysis of ammonia use 1 volume of concentrated ammonia water with 12.5 volumes of a saturated salt solution.

In the same way, equal quantities of chlorine are set free from all metallic chlorides, while the quantities of the precipitated metals agree with the values according to which they enter chemical action, their equivalent weight. The quantities of the different salts, decomposed by electrolysis, stand in the following relation :

$$AgNO_3, \frac{CuCl_2}{2}, \frac{Cu_2Cl_2}{2}, \frac{SbCl_3}{3}, \frac{FeCl_2}{2}, \frac{FeCl_3}{3}, \frac{SnCl_2}{2}, \frac{SnCl_4}{4}, \frac{CuSO_4}{2}, \frac{Hg(CN)_2}{2}, \frac{Hg_2(NO_3)_2}{2}.$$

Therefore, 31.8 parts of copper are deposited for the 35.45 parts of chlorine in cupric chloride, $CuCl_2$, but from cuprous chloride, Cu_2Cl_2, we obtain 63.6 parts of copper ; from mercuric cyanide, $Hg(CN)_2$, we obtain 100.15 parts of mercury, and from mercurous nitrate, $Hg(NO_3)$, 200.3 parts of mercury, etc.

These relations can be obliterated in that reductions of the electrolyte at the negative pole and its oxidation at the positive may occur through the decomposition products. Thus, in the electrolysis of cuprous chloride, cupric chloride instead of chlorine will be found at the anode :

$$CuCl + Cl = CuCl_2,$$

and in the electrolytic decomposition of cupric chloride cuprous chloride will appear at the kathode :

$$CuCl_2 + Cu = 2CuCl.$$

Some obscurity of the ratios acquired by the law also arises if the salt is hydrolytically decomposed, *e.g.*, if water converts it partly into hydroxide or basic salt, and free acid :

$$FeCl_3 + 3H_2O = Fe(OH)_3 + 3HCl ;$$

the free acid is also subject to electrolytic decomposition. Further, the proportions change if the electrodes are attacked by the substances liberated upon them (p. 77). For example, if in the electrolysis of copper sulphate the positive electrode consists of copper then oxygen will not be liberated here ($SO_4 = SO_3 + O$), but just as much metallic copper will dissolve as separates upon the kathode :

$$Cu + SO_4 = CuSO_4 ;$$

consequently the copper content of the solution remains unchanged.

H. Helmholtz accordingly expresses Faraday's law as follows:

The same quantity of electricity acting upon different electrolytes liberates equal valences or combines them in some new way.

Gauss and Weber referred most electrical and magnetic magnitudes to length (cm.), mass (gram) and time (sec.).

The units derived in this way are the absolute measurements. The unit quantity of electricity in this measurement precipitates, according to Kohlrausch, 0.01118 gram of silver. The tenth part of this quantity, or that which will precipitate 0.001118 gram = 1.118 mg. of silver, has been selected as the "practical unit" and is called the "coulomb" (coul.) ; 300 mg. of silver deposited upon the kathode indicate therefore that $\frac{300}{1.118} = 268$ coul. have passed through the solution. If this took place in ten minutes, then in one second $\frac{268}{600} = 0.447$ coul. would have passed through the liquid. The current strength would then have been 0.447 ampere. The current strength (amp.), therefore, represents the number of coulombs which pass through the entire cross-section of the current's course. A current of one ampere deposits or separates:

	Mg. Silver.	Mg. Copper.	Mg. Water.	C.c. Electrolytic Gas at 0° and 760 Mm.	C.c. Hydrogen at 0° and 760 Mm.
In one second, . .	1.118	0.3284	0.0933	0.1740	0.1160
In one minute, . .	67.08	19.70	5.60	10.44	6.960
In one hour, . .	4025	1182	335.9	626	417

The *electro-chemical equivalents* are the quantities which are separated out or converted into other compounds in the unit of time. It is possible in accordance with Faraday's law to calculate readily from the silver and copper values those of other elements or atomic groups. In general, a current of 1 ampere deposits in 1 sec. 0.01036, in 1 min. 0.6215, and in 1 hour 37.29 mg.—equivalents of any substance $\left(\frac{1.118}{107.93} = \frac{0.3284}{31.8} = 0.01036; \mathrm{Ag} = 107.93; \frac{\mathrm{Cu}}{2} = 31.8\right)$; hence, $35.45 \cdot 0.01036 = 0.3673$ mg. chlorine in a second, etc. It may also be mentioned that the practical unit of resistance, the *ohm*, is a column of mercury 106.3 cm. in length and 1 square mm. in section, and that the *volt*, the practical unit of electromotive force, is the power which in a closed circuit of an ohm resistance produces a current of 1 ampere.

Faraday's law requires that when equal quantities of electricity pass through different electrolytes, the same number of valences must be liberated or converted into new compounds at each pole. Therefore, the decomposition of aqueous hydrochloric acid is accomplished by the consumption of the same quantity of electricity which would be required by equivalent quantities of hydrobromic acid, hydriodic acid, etc. We know on the other hand that very different amounts of heat are necessary to effect the decomposition of equivalent quantities of these compounds. Hence we might expect that their electrolytic decomposition would demand a varying expenditure of electricity. The endothermic bodies should be most easily decomposed, while those with the greater heat of formation and heat of decomposition would be most difficult.

Furthermore, so long as the electric force, active in the conductor, is not equal in strength to the affinity, decomposition does not occur, but when these forces are equal, then many molecules will at once be broken down. This contradicts all experience which, according to R. Clausius, may be explained as follows [Pogg. Annalen (1857) **101**, 338; die mechanische Wärmetheorie (1879) Bd. II, 164]: The current does not decompose the electrolyte into its constituents. In consequence of the heat motions of its molecule the electrolyte is already partially dissociated and *the current merely separates the already free ions spacially.* Williamson, at an early date, had expressed a similar view in an unusually able paper on the theory of the ether-formation [Ann. Chem. Pharm. (1851) **77**, 37]. He thought that in a mass of molecules the latter continually exchanged the atoms and atom groups, of which they consisted, with one another. For example, in hydrochloric acid the molecule of hydrogen chloride did not constantly consist of the same hydrogen atom and chlorine atom, but that there was rather a mutual exchange of corresponding atoms among the molecules. S. Arrhenius has in late years expanded and developed these ideas into the theory of electrolytic dissociation, which will receive attention later, p. 268.

SOLUTIONS.

Most liquids can take up gases, other liquids and solids in such a manner that a new liquid, homogeneous both physically and chemically—a *solution*—is produced (p. 256). No deep-seated chemical changes occur between the solvent and the substance dissolved, otherwise the process could not be defined as solution in the sense indicated. If, for example, carbon dioxide is conducted into and absorbed by caustic potash, a solution of carbon dioxide does not result, but rather one of potassium carbonate. In the same way we cannot say that a metal dissolves in an acid, because it is first changed, with the evolution of hydrogen, into a salt which dissolves. Gases can mix to any degree with one another, but the solvent power of liquids for gases or other liquids or solids is generally limited and also dependent upon pressure and temperature. Aqueous solutions are alone important here, and only they will be considered now.

The absorption of gases (Henry, 1803) or gas mixtures (Dalton, 1807), as mentioned on p. 229, is proportional to the pressure under which the gas exists. The gas dissolved by a liquid can be expelled from it by raising the temperature, by lowering the pressure, or by introducing another gas, *e. g.*, carbon dioxide, by passing air through the solution, or by shaking the latter with air. Certain gas solutions are distinguished by the fact that under a definite pressure they will distil without change in their composition at a constant temperature; (see Hydrochloric Acid, p. 59, Hydrobromic Acid, p. 62).

Many metallic salts separate in union with water—*water of crystallization*—from their solutions. This can frequently be noticed in their change of color. Anhydrous copper sulphate, $CuSO_4$, is white, while its aqueous solution is blue, and on evaporation blue hydrous $CuSO_4 . 5H_2O$ crystallizes out. This salt loses a portion of its water, on exposure to the air, at the ordinary temperature—it *effloresces*. It becomes anhydrous above 200°. Hence, we can conclude that such a hydrate existed in the solution. In some cases the metallic salt, depending on the physical conditions at which the solution or crystallization occurred, unites with varying amounts of water, which is recognizable by its color. The compounds of cobaltous chloride, $CoCl_2$, with one and two molecules of water of crystallization are blue in color like the solution from which they separate, whereas the red compound with six molecules of water, $CoCl_2 + 6H_2O$, is obtained from red-colored solutions. As a rule, the solubility of salts increases with the rise in temperature and is definite for every temperature (*saturated solution*). Thus, 1 part of potassium nitrate dissolves in 4 parts of water at 15°, and in 0.3–0.4 parts at the boiling temperature. When such a hot saturated solution cools, the salt crystallizes out. Sodium chloride is a remarkable exception to this, as it dissolves very little more in hot than in cold water: 100 parts of water at the ordinary temperature take up 36 parts, and when boiling 39 parts of the salt. The solubility with other salts increases up to a definite temperature and then it diminishes. It is thus with sodium sulphate, Na_2SO_4; 100 parts of water at 0° dissolve five parts of the salt, and the most, namely 55 parts, at 34°; at 60° only 45 and at 100° about 42 parts (see Glauber's Salt). When a salt dissolves it absorbs heat and the water cools. However, if the salt, like anhydrous copper sulphate or calcium chloride, $CaCl_2$, can take up water, *i. e.*, able to form a hydrate, then heat is evolved in its solution, because the quantity of heat, set free in the formation of the hydrate, exceeds that necessary to dissolve it. Therefore, hydrated calcium chloride, $CaCl_2 + 6H_2O$, dissolves in water with the lowering of temperature.

THEORY OF DILUTE SOLUTIONS.

Many chemists regard solution as a chemical process induced by the chemical attraction between the solvent and the substance dissolved, and leading finally to very unstable and undetermined chemical compounds (Berthollet, Mendelejeff, Berthelot), while others believe it to be physical, *e. g.*, Dossios, who considers it a sort of diffusion, which may be compared in every respect to vaporization. Neither of the two views alone is sufficient to explain satisfactorily the process of solution [see Z. f. anorg. Ch. **6** (1894) 392].

While we cannot be certain as to the forces which bring about solution, yet since 1885 J. H. van't Hoff has by his pioneer researches shown that the condition of a substance in *dilute* solution is similar to the gas condition. The equation deduced on page 121:

$$pv = RT$$

embodies the law of gases (Boyle and Gay-Lussac) and that of Avogadro, and as proved by van't Hoff it also answers for dilute solutions if "osmotic pressure" be substituted for gas pressure [Z. f. phys. Ch. **1** (1887) 487; **3** (1889) 198; Ber. **27** (1894) 6].

Osmotic pressure is the pressure exerted against a diaphragm, separating a solution from a solvent, and which is permeable to the solvent but not to the dissolved substance (see p. 237). Changes brought about by osmotic pressure play a very important rôle in the living organism and particularly in plants, therefore they were first more accurately studied by botanists—W. Pfeffer in 1877 and H. de Vries in 1884.

The action of osmotic pressure may be demonstrated as follows: A cylinder of about 100 c.c. capacity is filled with a syrupy sugar solution and then made air-tight with a covering of animal membrane. When this vessel is immersed in a vessel of water, the membrane gradually forms a curved surface, because the water penetrates through it to the sugar solution. The experiment can also be conducted as follows: An open cylinder is closed at one end with a membrane and then filled with a concentrated sugar solution, the other end of the cylinder being provided with a stopper which carries a narrow glass tube. When the cylinder is immersed to the stopper in water, the latter penetrates the membrane and as a consequence the liquid rises gradually in the tube to a definite height; thus a means, though not very exact, is afforded for the measurement of the magnitude of the osmotic pressure.

Pfeffer and de Vries made measurements of osmotic pressure and found the following relations:

1. Osmotic pressure is proportional to the concentration or inversely proportional to the volume in which a definite amount of substance is dissolved.
2. Osmotic pressure increases with constant volume in proportion to the absolute temperature.
3. Quantities of dissolved substances, which are to one another as their molecular weights, exert equal osmotic pressure when dissolved in equal volume at like temperatures.

One of van't Hoff's services was the recognition that these three laws of osmotic pressure correspond to the laws controlling gases. The first is the counterpart of Boyle's law, the second, of the law of Gay-Lussac and Dalton, and the third corresponds to Avogadro's law.

Let us apply these relations to a solution which contains one part by weight of cane sugar in 100 parts by weight of water. In accordance with the specific gravity of such a solution it would contain 1 gram of sugar in 100.6 c.c. Pfeffer's experiments show that this solution exerts at 0° an osmotic pressure which would hold a mercury column of 49.3 cm. in height in equilibrium. If it is desired to ascertain whether these relations can be expressed by the equation $p . v = 84800\ T$, the units mentioned on p. 122 must be chosen and the pressure in grams per square centimeter, the volume in cubic centimeters for the gram-molecule and the temperature in absolute numbers must be considered in the calculation.*

In this particular instance the value for p would be $49.3 \cdot 13.6 = 670.48$; for T the value 273. Cane sugar, $C_{12}H_{22}O_{11}$, has the molecular weight 342.18; the gram-molecule of the solution in question is then contained in $342.18 \cdot 100.6 = 34400$ c.c. (v) approximately. Hence $670.48 \cdot 34400 = R \cdot 273$ and $R = 84500$, a value which accords within the limits of error with that of the gas constants.

Consequently dissolved substances exert the same pressure, as osmotic pressure, which they would exert at like temperature and like volume in the gas form. Their molecules are, as in the case of gases, so far removed from one another that only the properties dependent upon their number manifest themselves, while those depending upon composition and chemical structure ofttimes disappear absolutely. Properties of this kind, which can assume like values for chemically comparable quantities of the most different substances—for molecules, for atoms of bodies which are exceptions to Avogadro's law (p. 79), for ions, as we shall soon see, are termed, following Ostwald, *colligative properties* (*colligare*, to link together). The quantities of two substances, which in dilute solution or in the gas form manifest colligative properties of equal value, will be to one another as the ratio of their molecular weights if the exceptions indicated be not considered. It would then follow: that if at one time n-gram-molecules of a substance A be dissolved in a definite volume of a solvent, and then n-gram-molecules of the substance B, in both cases certain properties of the original solvent would be similarly altered. The freezing point will fall and the boiling point will rise regularly in both instances; the tension of the two solutions will be the same; they possess equal osmotic pressure, *i. e.*, they are *isotonic* (*ἴσος*, equal; *τόνος*, tension). It is in this manner possible, upon comparing solutions of a substance of unknown molecular weight with those of one of known molecular weight, to determine the unknown molecular weight: (1) by isotony (Pfeffer, de Vries); (2) by lowering of tension (Raoult); (3) by the rise in boiling point (Beckmann-Arrhenius); (4) by lowering of the freezing point (van't Hoff-Raoult-Eykmann). These methods are described in Richter's Organic Chemistry. To show how their properties change in proportion to concentration, mention may be made of the following: A solution of 1 part of common salt in 100 parts of water begins to freeze at —0.6°, one of 2 : 100 at —1.2°, of 4 : 100 at —2.4°, of 14 : 100 at —8.4°, *i. e.*, at $-0.6 \times 14°$. Below the last-named temperature the proportionality does not hold for anhydrous sodium chloride, but for the hydrate $NaCl + 2H_2O$. In the case of other salts the hydrates play this rôle at higher temperatures: thus, $NaI + 4H_2O$, $MgSO_4 + 7H_2O$, etc. [Rüdorff and de Coppet].

THEORY OF ELECTROLYTIC DISSOCIATION.

The laws just mentioned serve only for very dilute solutions, just as the laws for gases correspond with greater accuracy in the behavior of those gases which are far removed from the vapor condition (p. 122). And even very dilute solutions show deviations from van't Hoff's theory when the solvent is water and the dissolved substance is an electrolyte —a conductor of the second class (p. 262). The salts, acids and bases are electrolytes in aqueous solution, while the non-electrolytes are the organic compounds, with the exception of the pronounced acids, bases and salts; also the solutions of all substances in benzene, carbon bisulphide, ether, chloroform, etc. The alcoholic solutions constitute a transition to the electrolytes.

An example will illustrate these important relations. While the aqueous solutions of ether, glycol, sugar, urea and similar non-conducting organic compounds, which contain the molecular weight of the respective substances expressed in grams per liter, freeze at —1.8°, the freezing point of the corresponding solutions of potassium iodide, sodium chloride and silver nitrate falls to —3.6°, double the first; and that of such a solution of sodium sulphate to —5.4°, treble the first. The values of other colligative properties of these solutions manifest similar variations from the van't Hoff theory: rise in the boiling

---

* If the pressure be given in atmospheres and the volume in liters, then R naturally acquires another value. As the molecular volume (p. 98), at 1 atmosphere and 0°, equals 22.4 liters, then R would equal 0.082 (because $p = 1$, $v = 22.4$, $T = 273$): hence in general $p \cdot v = 0.082\,T$ (liter-atmosphere).

point, decrease in the vapor tension, and the osmotic pressure is also double or treble that required by the theory. Dilute solutions of electrolytes consequently behave as if they contained more molecules of the dissolved substance than the corresponding solutions of non-electrolytes.

Svante Arrhenius' theory of electrolytic dissociation [Z. f. phys. Ch. 1 (1887) 631; see also Planck, *ibid.* 576] offers an interpretation for this abnormal deportment. According to it the electrolytes—which Hittorf designates salt-like bodies inasmuch as the acids are salts of hydrogen and the bases of hydroxyl—do not exist as such in aqueous solution but have broken down entirely or in part into their ions (p. 265) — NaCl into $\overset{+}{Na}$ and $\overset{-}{Cl}$, $AgNO_3$ into $\overset{+}{Ag}$ and $\overset{-}{NO_3}$, Na_2SO_4 into $2\overset{+}{Na}$ and $\overset{-}{SO_4}$, and KOH into $\overset{+}{K}$ and $\overset{-}{OH}$. The anions are charged with negative and the kations with positive electricities which, in accord with the law of Faraday, are equally large for equivalent quantities of different ions, *e. g.*, the ion SO_4 contains twice the quantity of electricity of the ion Cl.

The ions regarded as independent mass-particles for comparison's sake play the part of molecules and accordingly influence the values of the colligative properties. This would explain the exceptions, cited above, to the theory of solutions; the molecule NaCl, resolved into the ions $\overset{+}{Na}$ and $\overset{-}{Cl}$, acts like two molecules; Na_2SO_4 separated into $2\overset{+}{Na}$ and $\overset{-}{SO_4}$ behaves like three molecules of a non-electrolyte. The determination of the lowering of the freezing point, etc., can therefore serve in determining the degree of dissociation. Dissociation and electric conductivity run parallel because the conduction of the current is influenced only by the presence of free ions and their quantity, whereas molecules which are not dissociated do not participate in conducting the current. Accordingly the conductivity actually increases, if molecular quantities be considered, with growing dilution and attains its maximum when all the molecules of the electrolyte are dissociated.

The neutral salts are most strongly dissociated and particularly those with univalent ions, *e. g.*, NaCl, $AgNO_3$, KI, NH_4Br. Usually more than half of the salt is present in the form of free ions in aqueous solutions at medium concentrations. Salts with polyvalent ions are less completely dissociated, and in the case of the mercury haloids the dissociation is extremely slight. The degree of dissociation with acids and bases corresponds to what is commonly called their "strength"; the strongest bases and acids are most completely dissociated. A gradual dissociation occurs with the polybasic acids: thus sulphuric first breaks down into the ions $\overset{+}{H}$ and $\overset{-}{HSO_4}$; the univalent anion HSO_4 in turn dissociates into $\overset{-}{SO_4}$ and $\overset{+}{H}$.

The *strong acids* would then be: Hydrochloric, hydrobromic, hydriodic, nitric, chloric, perchloric and sulphuric, as well as the polythionic acids. *Strong bases:* Alkalies, alkaline earths and the oxide of thallium. In solutions of medium concentration these compounds are dissociated more than half.

Moderately strong acids: Phosphoric, sulphurous and acetic. *Moderately strong bases:* Ammonia, magnesia and silver oxide (dissociation does not exceed 10 per cent.).

Weak acids and bases, the dissociation of which is in part scarcely measurable: Carbonic acid, hydrogen sulphide, hydrogen cyanide, silicic acid, boric acid—the hydroxides of the other bivalent and trivalent metals.

The formation of a salt from a base and an acid proceeds, according to this theory, in aqueous solution as follows: The base breaks down into the metallic kation and the anion OH, the acid into the kation H and the anion—the acid residue previously combined with it. Because water possesses an extremely slight degree of dissociation, being a non-conductor (a gram equivalent of its ions is contained in about 10,000,000 liters), it will be produced whenever the ions H and OH meet, so that in the present case, if we have started with equivalent quantities, only the ions of the salt will remain in solution:

$$\underbrace{\overset{+}{Na} + \overset{-}{OH}} + \underbrace{\overset{-}{Cl} + \overset{+}{H}} = \overset{+}{Na} + \overset{-}{Cl} + H_2O \,.\;.\;.\;.\;.\;.\;.\; + 13.7 \text{ Cal.}$$

$$\underbrace{K + OH} + \underbrace{NO_3 + H} = K + NO_3 + H_2O \,.\;.\;.\;.\;.\;.\;.\; + 13.7 \text{ Cal.}$$

$$\underbrace{Ca + 2OH} + \underbrace{2Cl + 2H} = Ca + 2Cl + 2H_2O \,.\;.\;.\;.\;.\;.\;.\; + 27.4 \text{ Cal.}$$

The common and essential thing in these changes is the production of water from the ions H and OH; the other ions remain unchanged as long as the concentration of the solution is not altered. A fact in harmony with this is that *upon neutralizing equivalent quantities of strong bases with strong acids an equal heat modulus* (thermal value) *is obtained;* hence,

$$(\overset{+}{\text{H}}\text{ aq.}, \overset{-}{\text{OH}}\text{ aq.}) = 13.7.$$

This fact, for which no reason could be previously observed, now seems in a similar manner to be demanded by and also to confirm the theory just discussed.

The salt-like bodies according to the theory of electrolytic dissociation appear to be binary in their constitution. Berzelius' old electro-chemical theory also made them consist of electro-positive and electro-negative parts—they were dualistically constituted. The salts of the oxygen acids consisted of the acid anhydride and the metallic oxide, *e.g.*, potassium sulphate of $\overset{-}{SO_3} . \overset{+}{K_2O}$—whereby they were brought in opposition to the haloid salts, which facts did not justify. The electro-chemical theory of Arrhenius proceeding from positive and negative constituents has a dualistic character, attaches itself thereby to the idea of Daniell and of Liebig (p. 260), and corresponds to the views to which Williamson and Clausius were led, the former for chemical and the latter for electrolytic reasons (p. 265). This theory at first appeared strange and met great opposition, but it is now almost universally accepted and it is generally admitted that we are indebted to it for many great and surprising discoveries in the domain of chemistry and physics which had gone unobserved. It appears almost absolutely necessary for young chemists to make themselves conversant with this theory and to that end the publications cited on pp. 49, 66 will be found helpful. The following will also prove especially valuable: Ostwald, Foundations of Analytical Chemistry; Lüpke, Elements of Electro-chemistry; Le Blanc, Electro-chemistry; Löb, The Elements of Electro chemistry; Windisch, Determination of the Molecular Weights.

TRANSPOSITION OF SALTS.

When two salts in solution or fusion come together, a chemical action will frequently occur. Claude Louis Berthollet (Essai de statique chimique, 1803) endeavored to explain the resulting phenomena by referring them to purely physical causes, and excluded chemical affinity.

In the opinion of Berthollet, four salts always arise in the solution of two. For example, on mixing solutions of copper sulphate and sodium chloride, there exist in solution copper sulphate, sodium sulphate, copper chloride, and sodium chloride:

$$n\text{CuSO}_4 + m\text{NaCl yield}$$
$$(n - x)\text{CuSO}_4 + (m - 2x)\text{NaCl} + x\text{Na}_2\text{SO}_4 + x\text{CuCl}_2.$$

That copper chloride is really present in the solution together with the sulphate, follows, from the fact that the blue color of the latter acquires a greenish color, peculiar to the copper chloride, by the addition of sodium chloride; other phenomena are not noticeable at first. Suppose one of the four salts formed in the solution is insoluble or volatile, the reaction will occur somewhat differently. Upon adding barium chloride to the copper sulphate solution four salts will be formed at the beginning just as in the first case. The barium sulphate produced separates, however, in consequence of its insolubility, the equilibrium of the four salts will be disturbed, and new quantities of copper sulphate and barium chloride act upon each other until the transposition is complete:

$$\text{CuSO}_4 + \text{BaCl}_2 = \text{BaSO}_4 + \text{CuCl}_2.$$

The chemical transposition may, therefore, be explained by the insolubility of the barium sulphate. On adding hydrochloric acid, or soluble chlorides, to the solution of a silver salt all the silver is precipitated as chloride, because the latter is insoluble.

Take another example. On adding sulphuric acid to a solution of potassium nitrate there is apparently no perceptible alteration; yet four compounds, KNO_3, $KHSO_4$, H_2SO_4 and HNO_3, are present in the solution. This was proved by the thermo-chemical investigations of Julius Thomsen, and from determinations made by W. Ostwald on the changes in volume and density which are connected with transpositions. The two acids distribute themselves upon the base. The proportion or degree to which this occurs is dependent upon the quantity of potassium nitrate and sulphuric acid in a volume unit, from external circumstances, such as the temperature, and upon the nature of reacting substances. The more sulphuric acid there is in proportion to the nitric, the more sulphate will there be formed. This is a case of *mass-action*, the theory of which was developed by Guldberg and Waage (p. 95). On heating or evaporating the nitrate solution containing sulphuric acid a new condition arises: the volatility of nitric acid. Hence it follows that on evaporation the transposition proceeds to completion in the sense of the equation:

$$2KNO_3 + 2H_2SO_4 = KHSO_4 + 2HNO_3.$$

These relations are thus explained by the theory of electrolytic dissociation. Neutral salts in dilute solutions do not as a rule act upon one another because, like the salts which can arise from them by transposition, they are equally dissociated. Thus a dilute solution of potassium chloride contains the ions K and Cl, that of sodium nitrate, the ions of Na and NO_3. If these solutions are mixed no change occurs. A solution of exactly the same properties would be obtained on mixing corresponding amounts of potassium nitrate and sodium chloride.

If a substance, less soluble and less dissociated under the prevailing conditions, can be formed from the ions, then a transposition, apparently an exchange, will occur. It is in this fashion that the transpositions described above are to be explained. The neutralization of bases by acids is to be accounted for in this way: water, which is but slightly dissociated, is formed from the ions H and OH, whereas the ions which belong to the salt remain (p. 269). The expulsion of a weak acid from its salts by a stronger acid is similarly completed. While the neutral salts are approximately equally dissociated, feeble acids on the other hand are changed but little. If therefore a strong acid be added to the solution of such a salt its hydrogen atoms will come together with the anions of the salt and will combine more or less completely with them to an acid which is not dissociated; there will remain the kation of the salt and the anion of the added acid, *e. g.*, hydrochloric acid and sodium borate:

$$\underbrace{\overset{-}{\mathrm{Cl}} + \overset{+}{\mathrm{H}}} + \underbrace{\overset{-}{\mathrm{BO_2}} + \overset{+}{\mathrm{Na}}} = \mathrm{HBO_2} + \underbrace{\overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}}}.$$

Salts of weak acids or of feeble bases are also hydrolytically decomposed by the action of water, *i. e.*, they break down into base and acid, of which the weak portion exists undissociated in the solution. The base or acid dissociated to a greater extent may be recognized by the fact that its solution reacts acid (with feeble base) or alkaline (with feeble acid).

The reactions employed to detect substances depend, according to the theory of electrolytic dissociation, chiefly upon reactions of ions. All compounds, for example, which in aqueous solution yield the anion Cl, show the reaction of hydrochloric acid, so far as they produce a precipitate of silver chloride with silver nitrate. When chlorine does not appear alone as an ion, but as a part of such, this reaction does not take place. The compound Na_2PtCl_6, the sodium salt of hydrochlorplatinic acid, rich in chlorine, does not yield a precipitate of silver chloride with silver nitrate, because in aqueous solution it dissociates into the anion $PtCl_6$ and the kations 2Na. The color of the solution is also materially affected by the ions. The following therefore is accordingly explained:

When ferric chloride and potassium fluoride meet in solution in equivalent amounts a whole series of characteristics belonging to ferric chloride solutions disappear: the solution is colorless; iodine is not set free from potassium iodide even after the addition of an acid; potassium sulphocyanide, salicylic acid and substances which otherwise detect ferric chloride with great accuracy, fail to show anything. Formerly there was no explanation for the deep-seated transposition which had evidently occurred in the liquid, but it may be found according to the theory of electrolytic dissociation in the fact that ferric chloride and potassium fluoride are completely transposed to ferric fluoride and potassium chloride:

$$FeCl_3 + 3KFl = 3KCl + FeFl_3,$$

and ferric fluoride is not dissociated. The trivalent iron ions, upon which the reactions recorded above are dependent, are no longer present in the solution; therefore, the reaction cannot occur. This transposition completes itself so fully that it can be applied in the quantitative determination of fluorides by working with an excess of ferric chloride and then determining the portion, not converted into fluoride, with potassium iodide, upon which ferric fluoride does not act (Knobloch). Similar relations will be cited in the following pages.

I. GROUP OF THE ALKALI METALS.

Potassium,	39.15	Lithium,	7.03
Rubidium,	85.4	Sodium,	23.05
Cæsium,	133	(Ammonium, NH_4 = 18.07)	

The metals of this group are decidedly the most pronounced in metallobasic character, and this constitutes a visible contrast with the elements of the chlorine group, the most energetic among the acid-forming metalloids.

The alkali metals in physical and chemical properties exhibit great similarity. They oxidize readily in the air, decompose water violently, even in the cold, with the formation of strong basic hydroxides, which dissolve readily in water and are called *alkalies* (caustic potash, caustic soda); hence the name alkali metal (*al kaljun*, Arabic, meaning the ash of sea and beach plants, and the extract from the same). They are not decomposed by ignition. Their chemical energy increases with increasing atomic weight (more correctly atomic volume), sodium is more energetic than lithium, potassium more than sodium, and rubidium more than potassium. Cæsium has not been studied in the free condition, but, judging from its compounds, it possesses a more basic character than rubidium. We saw in other analogous groups (of chlorine, oxygen, phosphorus, carbon, and similar elements), that the metalloidal, electro-negative character diminishes, and the basic increases with the increasing atomic weight.

The specific gravities increase simultaneously with the atomic weights; but as the increase of the latter is greater than that of the former, the atomic volumes (the quotients $\frac{A}{\text{sp. gr.}}$, p. 252), are always greater. The increasing fusibility and volatility correspond to the increase of the atomic volumes; rubidium distils at a red heat, while lithium volatilizes only with difficulty:

	Li	Na	K	Rb	Cs
Atomic weight,	7.03	23.05	39.15	85.4	133
Specific gravity (15°),	0.59	0.97	0.87	1.52	1.88
Atomic volume,	11.9	23.7	45	56.1	70.7
Fusion temperature,	180°	96°	62.5°	38.5°	26.5°
Boiling temperature,	. .	742°	667°	. .	270°

Although the alkali metals exhibit a great similarity in their chemical deportment, we discover more marked relations between potassium, rubidium and cæsium upon the one hand, and lithium and sodium on the other, which accords with their position in the periodic system of the elements (p. 246). Especially is this noticed in the salts. The first three metals form difficultly soluble tartrates and chlorplatinates (see Platinum). Their carbonates deliquesce in the air, while those of sodium and lithium are stable under similar circumstances; the last is, indeed, rather insoluble in water. The phosphates deport themselves similarly; lithium phosphate is very difficultly soluble. It must be remarked that the normal carbonates and phosphates of all other metals are insoluble in water. In lithium, then, which possesses the lowest atomic weight, it would seem the alkaline character has not reached its full expression, and it in many respects approaches the elements of the second group, especially magnesium, just as beryllium approaches aluminium. The elements of the two small periods (lithium and sodium) are, indeed, similar, but not completely analogous, while the homology of the three great periods finds expression in potassium, rubidium and cæsium.

Of the thermo-chemical relations of the alkali metals only the heat of formation of some hydrates will be given here:

$$(Li, O, H, Aq) = 117.4 \quad (Na, O, H, Aq) = 111.8 \quad (K, O, H, Aq) = 116.4.$$

On comparing these values with the heat of formation of water $(H_2, O) = 68.36$ Cal., we immediately perceive why it is so readily decomposed by the alkali metals. All metals, disengaging more than 68.3 Cal. in the formation of their oxides, Me_2O, or their hydroxides, MeOH, decompose water, and the energy will be greater, the greater the difference of heat. The insolubility of the oxides constitutes an obstacle to the action; this, however, may be removed (see Aluminium) by addition of neutral solvents. Conversely, all oxides, affording less heat in their formation, are easily reduced by hydrogen (pp. 92, 95).

---

1. POTASSIUM.

$K = 39.15.$

In nature, potassium is found principally in silicates, viz.: feldspar and mica. By the disintegration of these frequently occurring minerals, potassium passes into the soil, and is absorbed by plants; the ashes of the latter consist chiefly of different potassium salts. The chloride and sulphate are also found in sea-water, and in large deposits in Stassfurt, at Magdeburg, and in Brunswick and in Galicia, where they were left by the evaporation of the water of inclosed seas.

Metallic potassium was first obtained by Davy, in the year 1807, by the decomposition of the hydroxide, by means of a strong galvanic current. At present it is prepared by igniting an intimate mixture of carbon and potassium carbonate:

$$K_2CO_3 + 2C = 2K + 3CO.$$

Such a mixture may be made by the carbonization of organic potassium salts, *e. g.*, crude tartar. It is then ignited to white heat, in an iron retort, and the escaping vapors collected in receivers of peculiar construction, filled with rock oil. The latter, a mixture of hydrocarbon, serves as the best means of preserving potassium, which would otherwise oxidize in the air, and decompose other liquids. Potassium carbon monoxide $(KCO)_6$ is a by-product in the preparation of the metal; see Richter's Organic Chemistry.

In a fresh section, potassium shows a silver-white color and brilliant metallic luster. At ordinary temperatures it is soft, like wax, and may be easily cut. It crystallizes in octahedra, and has a specific gravity of 0.87 at 15°. It melts at 62° and boils at about 667°, and when raised to a red heat, is converted into a greenish vapor. It oxidizes in the air, and becomes dull in color; heated, it burns with a violet flame. It decomposes water energetically, with formation of potassium hydroxide and the liberation of hydrogen. If a piece of the metal be thrown upon water, it will swim on the surface with a rotary motion; so much heat is disengaged by the reaction that the generated hydrogen and the potassium inflame. Finally, a slight explosion usually results, whereby pieces of potassium are tossed here and there; it is advisable, therefore, to execute the experiment in a tall beaker glass, covered with a glass plate. Potassium combines directly and very energetically with the halogens.

On conducting hydrogen over metallic potassium heated to 300–400°, potassium hydride, K_2H (or K_4H_2), results. This is a metallic, shining, brittle compound, which, upon stronger heating (above 410°), more readily *in vacuo*, is again decomposed. The sodium hydride, Na_4H_2, obtained in the same way, does not ignite spontaneously, but in other respects is very much like *potassium hydride.*

The influence of heat and pressure in the formation and decomposition of these compounds is very noteworthy. If, for example, potassium hydride be heated it melts, but otherwise remains unchanged. Above 200° (in a vacuum) it sustains a partial decomposition (dissociation), which gradually increases as the temperature rises. If the heating should take place in a closed vessel provided with a manometer, it will be observed that the decomposition at a given temperature will continue until the liberated hydrogen has acquired a definite tension—until it exerts a definite pressure. For potassium hydride, this tension, at 330°, equals 45 mm. The decomposition will then cease, but will proceed further at the same temperature if the hydrogen gas be removed, until the pressure of 45 mm. is again reached. This pressure is therefore called the *dissociation tension.* In this manner a complete decomposition of the hydride may be effected at the temperature given above. If, however, the disengaged hydrogen is not removed, but be added to the completely or partially decomposed hydride, and the pressure be raised to 45 mm. (at the temperature 330°), the potassium hydride will be re-formed. Consequently, both the decomposition and the formation of a body can follow, depending upon whether the external partial pressure be lowered or increased. Similar phenomena occur at higher temperatures, the corresponding pressure, of course, increasing by regular steps.

The tension of dissociation is independent of the relative quantity of the dissociated body and of the space which the disengaged gas can occupy, whereas in solutions and absorptions (ammonia by charcoal) the pressure at one and the same temperature increases with the quantity of the absorbed gas.

All exothermic compounds behave like potassium and sodium hydrides when they are decomposed into their components; if the pressure be raised above the tension of dissociation the components reunite—the compounds are re-formed. The decomposition of the endothermic compounds (potassium chlorate into chloride and oxygen) is quite different (pp. 30, 94). It proceeds with heat disengagement ($KCl,O_3 = -9.8$ Cal.), corresponding to the chemical affinities, and is only induced by application of external heat. It is independent of external pressure, and there is no reunion of the decomposition products upon increasing the external pressure or upon lowering the temperature.

We must not omit mentioning the great analogy between the phenomena of dissociation and the vaporizing of liquids. Like dissociated bodies, liquids exhibit at all temperatures a definite vapor tension. If the pressure above the liquid be diminished the evaporation will continue until the vapor tension is regained, but if the pressure be increased then a corresponding portion of the vapor will be condensed.

Oxygen compounds of potassium are not known in a pure state. The metal is not attacked by pure, dry oxygen below 60–80°. Above this temperature it burns in the gas, if its surface be renewed, to a yellow mass which, according to Erdmann and Köthner, consists of the sesquioxide, K_2O_3, and superoxide, KO_2. The oxide K_2O, from which the potassium salts are derived, is not definitely known.

Potassium Hydroxide, or *Caustic potash* (*Kalium causticum*), KOH, is obtained by the action of potassium or its oxide upon water. For its preparation, potassium carbonate is decomposed by calcium hydroxide (slaked lime):

$$K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2KOH.$$

The solution of 1 part of potassium carbonate in 10–12 parts of water is boiled with 1 part of slaked lime in an iron pot until a filtered portion does not effervesce, when hydrochloric acid is added; *i. e.*, until there is no longer any carbonic acid present. On standing awhile, the insoluble calcium carbonate subsides, and the liquid becomes clear. The solution of potassium hydroxide is then poured off, evaporated, the residue melted in a silver dish (which it does not attack), until the hydroxide begins to volatilize in clouds, when it is poured into moulds (*K. causticum fusum*). The caustic potash, prepared in this way, is not entirely pure, but contains potassium chloride and other salts. To obtain a product that is chemically pure, fuse potassium nitrate with copper filings, and evaporate the aqueous extract of the fusion in silver vessels.

One of the most brilliant achievements of modern chemical industry is *the electrolytic decomposition of the chlorides of the alkali metals into free chlorine and metal;* the latter at the moment of its liberation is converted by water into its hydroxide. The practical solution of this problem has made this operation a technical process since 1890. The Stassfurt potassium chloride has been thus made to yield pure caustic in solution and in solid form; also chlorine, bleaching lime and hydrogen (pp. 51, 278; also under Soda).

Potassium hydroxide forms a white, crystalline mass which fuses rather easily, and volatilizes undecomposed at a very high temperature. Exposed to the air it deliquesces, as it absorbs water and carbon dioxide. It is very soluble in alcohol, and especially in water. The solution (*Liquor kalii caustici*) possesses a strong alkaline reaction, saponifies the fats, and has a corrosive action upon the skin and organic tissues. At low temperatures the hydrate $KOH + 2H_2O$ crystallizes out from concentrated solutions.

The haloid salts of potassium are obtained by the direct union of the halogens with potassium, and by the saturation of the hydroxide or carbonate with haloid acids. They are readily soluble in water, have a salty taste, and crystallize in cubes. When heated they melt, and are somewhat volatile.

Potassium Chloride (*K. chloratum*), KCl, occurs in Stassfurt in large deposits, as *sylvite*, and combined with magnesium chloride exists as *carnallite* ($MgCl_2$, $KCl + 6H_2O$).

The opening up and the practical yields of the Stassfurt salt beds containing carnallite; kieserite, $MgSO_4 . H_2O$; tachhydrite, $CaCl_2 . 2MgCl_2 + 12H_2O$; kainite, $MgSO_4 . K_2SO_4 . MgCl_2 + 6H_2O$; boracite, $2Mg_3B_8O_{15} + MgCl_2$, and also bromides (p. 53) have been of great commercial importance to the German Empire. These are the largest salt-beds in the world. Before they were worked very considerable quantities of salt were imported into Germany but now that country stands at the head of all the salt-producing portions of the earth. In 1897 Stassfurt yielded 273,364 tons of rock-salt ($277,026) and 1,946,188 tons of crude potash salts ($6,513,553); in the same year the production of potassium chloride in the German Empire amounted to 108,000 tons ($5,764,423).

Carnallite serves as the chief source for the preparation of potassium chloride; water decomposes it into the more sparingly soluble potassium chloride and the readily soluble magnesium chloride. It is interesting to note that three-fourths of the potassium chloride separate in solid form when carnallite is heated to 176°. The liquid separated from this yields carnallite again on cooling to 115°, while magnesium chloride remains dissolved. The chloride crystallizes in vitreous cubes, of specific gravity 1.98. It melts at about 800°, and volatilizes at a strong red heat [see Jahrbuch der Chemie v (1895), 66, 67]. 100 parts of water dissolve 29 parts of the salt at 0°, and 56 parts at 100°. Potassium chloride is used in making nearly all the other potassium salts, hence it is largely applied technically (see Potassium Carbonate, Potassium Nitrate, Potassium Chlorate).

Potassium Bromide (*K. bromatum*), KBr, is generally obtained by warming a solution of potassium hydroxide with bromine, when the bromate is also produced:

$$6KOH + 3Br_2 = 5KBr + KBrO_3 + 3H_2O.$$

The solution is evaporated to dryness, mixed with charcoal, and ignited, which reduces the bromate to bromide:

$$KBrO_3 + 3C = KBr + 3CO.$$

It is readily soluble in water and slightly in alcohol; forms cubes of specific gravity 2.4, and melts at about 740°.

Potassium Iodide (*K. iodatum*), KI, may be prepared like the preceding. The iodate produced along with the iodide upon adding iodine to caustic potash may be reduced by hydrogen peroxide:

$$KIO_3 + 3H_2O_2 = KI + 3H_2O + 3O_2 \text{ (p. 180).}$$

It is usually obtained according to the following method: Iodine (3 parts) and iron filings (1 part) are rubbed together under water; an equal quantity of iodine (1 part) is again added to the solution of this ferrous iodide, FeI_2, in order to form ferrous-ferric iodide, Fe_3I_8, which is then boiled with the required quantity of potassium carbonate; this will precipitate ferrous-ferric oxide; carbon dioxide escapes, and potassium iodide will be found in the solution:

$$Fe_3I_8 + 4K_2CO_3 = Fe_3O_4 + 8KI + 4CO_2.$$

It forms large white crystals, fuses at about 720°, and is tolerably volatile. Its specific gravity equals 3.0. At medium temperatures it dissolves in 0.7 part of water and 2.5 parts of absolute alcohol. The aqueous solution dissolves iodine in large quantity. Many metallic, insoluble iodides dissolve in it without difficulty, forming double iodides, *e. g.*, $HgI_2 . 2KI$. The iodide is employed in medicine and in photography.

Potassium Fluoride, KFl, is obtained by dissolving the carbonate in aqueous hydrofluoric acid. It crystallizes in cubes at ordinary temperatures, with two molecules of water, but above 35° does not contain water of crystallization. It is very soluble in water. The aqueous solution attacks glass. It is greatly inclined to combine with other fluorides: KFl . HFl; $BFl_3 . KFl$. The commercial salt is frequently rich in arsenic. On adding hydrofluosilicic acid to the solution of potassium salts, a gelatinous precipitate of potassium silico-fluoride, K_2SiFl_6, is thrown down, which dissolves with difficulty in water.

Potassium Cyanide, KCN. This salt can be produced by saturating potassium hydroxide with hydrocyanic acid, and by heating yellow prussiate of potash (see Iron). It forms a white, easily fusible mass, which deliquesces in the air. The solution may be easily decomposed. The salt crystallizes in cubes, has an alkaline reaction, and smells like prussic acid. As the result of hydrolysis free prussic acid—which is very slightly dissociated—is present with free alkali. The introduction of carbon dioxide completes the decomposition. By fusion potassium cyanide reduces many metallic oxides, and hence is employed in reduction processes. It is just as poisonous as prussic acid. It is applied in many ways, especially in photography and for galvanic silvering and gilding. Lately it has met with extended application in the extraction of gold from low-grade ores and from sand. Generally it is a mixture of potassium and sodium cyanides which is used for this purpose; this can be obtained by fusing potassium ferrocyanide with sodium:

$$K_4Fe(CN)_6 + 2Na = 2NaCN + 4KCN + Fe.$$

Potassium Chlorate (*K. chloricum*) $KClO_3$, is produced when a slight excess of chlorine is introduced into caustic potash, and the hypochlorite, formed at first, oxidized thereby to chlorate. This change proceeds most rapidly at 80–90° (see p. 178). The sparingly soluble chlorate separates when the solution cools.

Technically, a solution of calcium chlorate, produced by slightly supersaturating lime-water with chlorine at 40°, is mixed with a sufficient quantity of potassium chloride, when potassium chlorate and calcium chloride result:

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$

Magnesia can be advantageously substituted for lime-water.

At present this old method of Liebig is being more and more supplanted by the electrolytic method, particularly since Oettel found that potassium chlorate is formed electrolytically in alkaline solutions of potassium chloride without the use of a diaphragm, which separated the anode from the kathode liquor. Since the electrolysis of potassium chloride yields caustic (together with hydrogen) at the kathode and chlorine at the anode, the conditions for the production of chlorate are evident. See also Elbs, Chem. Zeit. 1897, 996.

A French company in Switzerland first made chlorate electrolytically, while the caustic alkalies were first produced in this way in Germany; England followed later. The technical manufacture of electrolytic chlorate has been in operation since 1891 in Switzerland. The chemical factory at Griesheim began to make caustic potash and soda electrolytically in 1890. Since 1894 the electric factory at Bitterfeld has produced chiefly caustic and bleaching liquors in the electrolytic way. Other companies have followed those mentioned, and by some of them soda is now being prepared from electrolytic caustic soda.

Potassium chlorate crystallizes from the hot solution in shining tables of the monoclinic system, which dissolve with difficulty in cold water (100 parts at the ordinary temperature dissolve 6 parts of the salt). Its taste is cooling and astringent. When heated it melts at 360° and at higher temperatures gives up a portion of its oxygen, and changes to the chloride and **Perchlorate**, $KClO_4$, which on further heating decomposes into oxygen and potassium chloride (see p. 178). With hydrochloric acid it liberates chlorine:

$$KClO_3 + 6HCl = KCl + 3H_2O + 3Cl_2.$$

Mixed with sulphur, or certain sulphides, it explodes on heating and when struck a sharp blow. The igniting material upon the so-called Swedish (parlor) matches consists of antimony sulphide and potassium chlorate; when this is rubbed upon the friction surface coated with red phosphorus it ignites.

Potassium Hypochlorite, $KClO$, is formed when chlorine is conducted into a solution of potassium hydroxide:

$$2KOH + Cl_2 = KCl + KClO + H_2O.$$

It only exists in aqueous solution; when the latter is evaporated the salt is decomposed into chloride and chlorate:

$$3KClO = 2KCl + KClO_3.$$

In the presence of an excess of chlorine chlorate is rapidly produced.

The solution has an odor resembling that of chlorine, and bleaches strongly, especially upon the addition of acids (p. 175). The bleaching solutions occurring in trade (Eau de Javelle) are prepared by the action of chlorine upon solutions of sodium (Eau de Labarraque) and potassium (Eau de Javelle) carbonates; but recently they have been made by the electrolysis of the corresponding chlorides. They also contain free hypochlorous acid.

The oxy-salts of bromine and iodine are perfectly analogous to those of chlorine. *Potassium bromate*, $KBrO_3$, and *Potassium iodate*, KIO_3, are prepared by the action of bromine or iodine upon hot potassium hydroxide; the second is also produced by the action of iodine upon potassium chlorate, when the chlorine is directly replaced (p. 180). The experiments of Klinger and of Bassett apparently prove that a direct replacement of chlorine by iodine does not take place here; it is rather the oxidation of the latter by the anion ClO_3 of the chlorate. Potassium iodate can also be made by oxidizing potassium iodide (1 part) with potassium permanganate (2 parts) in aqueous solution. If chlorine be passed through a hot solution of potassium iodate or iodide in potassium hydroxide, the periodate of potassium, KIO_4, arises; it is difficultly soluble and when heated decomposes into oxygen and potassium iodate, which then breaks down into potassium iodide and oxygen.

Besides the normal periodates, KIO_4, $NaIO_4$, other salts exist which are derived from the highest hydroxyl compound, $I(OH)_7$, and its anhydro-derivatives (p. 181). These salts are very numerous, and are in part monoperiodates, $IO(OH)_5$ and $IO_2(OH)_3$, and partly polyperiodates, produced by the condensation of several molecules of the highest hydroxides with the exit of water, *e. g.*, $I_2O_3(OH)_8$, $I_2O_5(OH)_4$, and $I_2O_6(OH)_2$.

Potassium Sulphate, K_2SO_4, is formed in the action of concentrated sulphuric acid upon potassium chloride, and as a by-product in many technical operations. It is also obtained by transposing schönite, $MgSO_4.K_2SO_4 + 6H_2O$, and other Stassfurt salts containing sulphates with potassium chloride:

$$MgSO_4.K_2SO_4 + 2KCl = 2K_2SO_4 + MgCl_2.$$

It crystallizes without water, in small rhombic prisms, having a bitter, salty taste, and dissolves in 10 parts of water at the ordinary temperature. It melts at about 1070°. It is employed principally for the preparation of potassium carbonate, according to the method of Le Blanc (p. 281).

The *acid* or *primary salt*, $KHSO_4$, crystallizes in large rhombic tables, and is very readily soluble in water. It fuses at about 200°, loses water, and is converted into potassium pyrosulphate, $K_2S_2O_7$, which at 600° yields K_2SO_4 and SO_3 (p. 194).

Potassium Sulphite.—The salts of sulphurous acid—the *primary*, $KHSO_3$, and the *secondary sulphites*, K_2SO_3—are produced when sulphuric dioxide comes in contact with a potassium carbonate solution; they are very soluble and crystallize with difficulty. The first salt shows an acid, the second an alkaline reaction. If sulphur dioxide be passed into a solution of potassium carbonate until effervescence ceases and then cooled, the pyrosulphite, $K_2S_2O_5$, corresponding to the pyrosulphate, will crystallize out.

Potassium Persulphate, $K_2S_2O_8$, results on electrolyzing a saturated solution of acid potassium sulphate, when it separates at the anode as a white crystalline precipitate. It can be crystallized from hot water; on rapid cooling it separates in small prisms. Its solution oxidizes, has a cooling, salt-like taste and does not yield a precipitate with solutions of other metals (the salts of silver, manganese and cobalt excepted). The dry salt commences to decompose at 100° into oxygen and pyrosulphate (see p. 188).

Potassium Nitrate, *Saltpeter* (*K. nitricum*), KNO_3, occurs in the largest amounts in East India, especially in Ceylon, at Bengal and at Gutscharat (Bombay) in distinct layers; in cavities (in Ceylon) once the lairs of animals and of men's dwelling-places, which are even now inhabited by hosts of field mice. It is found in abundance in other torrid regions in the soil, upon which it effloresces during the dry season (hence *sal*, salt; *πετρα*, rock), *e. g.*, in Peru, in Bolivia, in South Africa, also in Egypt, etc. It is produced wherever nitrogenous organic substances decay in the presence of potassium carbonate (aided by micro-organisms), conditions which are present in almost every soil. The intentional introduction of these is the basis of the artificial niter production in the so-called saltpeter plantations, which were formerly cultivated actively in Spain, Hungary, Sweden and Switzerland. Manures and various animal offals are mixed with wood ashes (potassium carbonate) and lime, arranged in porous layers, and submitted to the action of the air (protected from rain) for two or three years, when nitrates are produced from the slow oxidation of the nitrogen. The heaps are then treated with water and potassium carbonate added to the solution, which contains potassium, calcium and magnesium nitrates, to convert the last two salts into potassium nitrate :

$$Ca(NO_3)_2 + K_2CO_3 = CaCO_3 + 2KNO_3.$$

The precipitate of calcium and magnesium carbonates is filtered off and the solution evaporated. The soils of East India containing niter are similarly worked. Until the Crimean War (1852–1855) the demand for potassium nitrate in manufacturing gunpowder was met almost exclusively by East India. The numerous and constant inquiries for the salt led German chemists to transpose the Chili salpeter by means of Stassfurt potassium chloride into the potassium salt (conversion saltpeter):

$$NaNO_3 + KCl = NaCl + KNO_3.$$

Warm saturated solutions of equivalent quantities of sodium nitrate and potassium chloride are mixed and boiled, when sodium chloride, being less soluble in hot water, will separate. On cooling the solution potassium nitrate, being less soluble in cold water, crystallizes out; sodium chloride is about equally soluble in hot and cold water, for which reason the portion not separated by boiling remains in solution (p. 266).

Potassium saltpeter crystallizes without water of crystallization in large, six-sided rhombic prisms. It is far more soluble in hot than in cold water; 100 parts of water dissolve 247 parts at 100°, but at 0° only 13 parts. It possesses a cooling taste, fuses at 340°, and decomposes, when further heated, into oxygen and potassium nitrite, KNO_2. Heated with carbon it yields potassium carbonate:

$$4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2.$$

Its principal use is in the manufacture of gunpowder. This is a granular mixture of potassium nitrate, sulphur, and charcoal. The relative quantities of these constituents are somewhat different in the various kinds of powder (sporting, blasting, and powder free from sulphur). The first consists of $4KNO_3 + 2C + 2S = 2K_2SO_4 + 2CO_2 + 2N_2$; the second: $4KNO_3 + 6C + 4S = 2K_2S_2 + 6CO_2 + 2N_2$, and the third: $4KNO_3 + 5C = 2K_2CO_3 + 3CO_2 + 2N_2$. These three varieties, mixed in different but simple proportions, constitute the powders in general use. Each variety possesses peculiarities as to ignition, combustibility, energy content, heat and gas content. The mixing is made in accordance with the demand for any one or more of these properties. The effectiveness of the powder, therefore, depends upon the disengagement of carbon dioxide and nitrogen gas, the volume of which is almost 1000 times as great as that of the decomposed powder.

Potassium Nitrite (*K. nitrosum*), KNO_2, is obtained by fusing saltpeter with lead (2 parts) which withdraws one atom of oxygen from the former (p. 205). It forms a white, crystalline, fusible mass, which deliquesces in the air.

Potassium Phosphates.—The potassium salts of *phosphoric acid:* K_3PO_4, K_2HPO_4, and KH_2PO_4, meet with no practical application, they are readily soluble in water and crystallize poorly; therefore, the sodium salts are generally used. The borates, KBO_2 and $K_2B_4O_7 + 5H_2O$ (see Borax), crystallize with difficulty.

Potassium Carbonate, K_2CO_3, ordinarily known as **potashes**, is the principal ingredient of the ashes of land plants.

As 1000 parts of wood yield 3.5–28 parts of ashes and the potassium carbonate in the latter is 0.45–4 parts it is obvious that only countries like Russia, Canada, the United States, Hungary and Galicia where there is an abundance of woodland can produce potashes in large amounts from the wood ashes. The latter are extracted with water, the clear filtrate is then evaporated until it solidifies on cooling, when the residue is dehydrated and decolorized by calcination in ovens. The product is *crude potashes*. By repeating the preceding treatment *purified potashes* or *pearl ash* is obtained. In countries like Belgium, Germany, France and Switzerland where sugar beets are cultivated large quantities of potassium carbonate are separated from the ash of the beets. Beets withdraw large quantities of potash salts from the soil which if the latter is to remain fertile must be returned to it by potash fertilizers. In this direction the Stassfurt potash salts are most valuable. The alkali salts of the beet are in its juice and they remain, when the sugar is extracted from the latter, in the *molasses*. When the latter is allowed to ferment, then evaporated and subjected to dry distillation, alcohol, ammonia, trimethylamine and other valuable substances are obtained; furthermore, the residual coke is rich in potash. Its aqueous extract is worked for potassium carbonate. Sheep's suint contains potassium salts of organic acids which on incineration yield potassium carbonate. The same salt is obtained as a by-product in the manufacture of iodine and bromine from sea-algæ and sea-weeds.

In Germany all these methods for the preparation of potassium carbonate give place to those in which the Stassfurt potassium chloride is utilized, from which potassium carbonate is prepared by two methods:

1. *Method of Le Blanc.*—This will be discussed in connection with soda. H. Grüneberg was the first to employ it in making potashes.

2. *Method of Ch. R. Engel* in Montpellier.—Precht introduced this method into German industries. Magnesium carbonate is mixed with a solution of potassium chloride, and the liquid, while being stirred, is saturated with carbon dioxide. A double salt of magnesium carbonate and acid potassium carbonate separates while the solution contains magnesium chloride:

$$3MgCO_3 + 2KCl + CO_2 + 9H_2O = 2[MgCO_3 . KHCO_3 . 4H_2O] + MgCl_2.$$

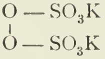
The double salt is freed from any adherent liquor by washing it with a solution of magnesium bicarbonate, after which it is decomposed under pressure with water at 140°. Basic magnesium carbonate separates in a compact form; carbon dioxide escapes, and the liquid containing pure potashes is evaporated and the residue calcined. Potassium carbonate free from sodium salts can be obtained in this way, because sodium chloride does not act upon magnesium carbonate.

The commercial carbonate is a white, granular, deliquescent powder, melting at 890°, and vaporizing at a red heat. It crystallizes from concentrated aqueous solutions with 1½ molecules of water, in monoclinic prisms; at 100° it loses ½ molecule of water. The solution has a caustic taste and shows an alkaline reaction. When carbon dioxide is conducted through the liquid it is absorbed and *primary potassium carbonate* is produced:

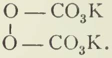
$$K_2CO_3 + H_2O + CO_2 = 2KHCO_3.$$

This salt, ordinarily called *bi-carbonate,* crystallizes in monoclinic prisms, free from water. It dissolves in 3–4 parts of water and exhibits a neutral reaction. When heated, it decomposes into potassium carbonate, carbon dioxide, and water. The decomposition of the dry salt does not begin until at about 110°, while the aqueous solution decomposes even on evaporation. Potassium carbonate is used almost entirely in the production of Bohemian or crystal glass.

Constam and v. Hansen electrolyzed solutions of potassium carbonate, cooled to —15°, and obtained at the anode **Potassium Percarbonate**, $K_2C_2O_6$,—a slightly blue-colored, deliquescent powder. It is formed, like the persulphates, by the union of the ions KCO_3, into which (together with potassium ions) the carbonate is decomposed by the current. It resembles the persulphates in properties, in so far that when heated to 200–300° it rapidly decomposes into carbonate and oxygen. Oxygen escapes from its aqueous solution at 45°. It is a powerful oxidant; many dyes are bleached by it. Dilute acids evolve hydrogen peroxide from it: $K_2C_2O_6 + 2HCl = 2CO_2 + 2KCl + H_2O_2$; this also occurs with caustic potash: $K_2C_2O_6 + 2KOH = 2K_2CO_3 + H_2O_2$. Its solution rapidly reduces manganese peroxide, lead peroxide and silver oxide with energetic liberation of oxygen: $Ag_2O + K_2C_2O_6 = Ag_2 + K_2CO_3 + CO_2 + O_2$. See p. 102. Its chemical structure is very likely analogous to that of the persulphates (pp. 188, 189, 279):



$$\begin{array}{l} O - SO_3K \\ | \\ O - SO_3K \end{array}$$



$$\begin{array}{l} O - CO_3K \\ | \\ O - CO_3K. \end{array}$$

Potassium Silicate, water-glass, does not possess a constant composition and cannot be obtained crystallized. It is produced by solution of silicic acid or amorphous silicon dioxide in potassium hydroxide, or by the fusion of silica with potassium hydroxide or carbonate. The concentrated solution dries in the air to a glassy, afterward opaque, mass, which, when reduced to a powder, will dissolve in boiling water. Potassium (and also sodium) water-glass has an extended application, especially in cotton printing, for the fixing of colors (stereochromy), in rendering combustible material fireproof, in soap boiling, etc.

SULPHUR COMPOUNDS OF POTASSIUM.

Potassium Hydrosulphide, KSH, is obtained when potassium hydroxide is saturated with hydrogen sulphide:

$$KOH + H_2S = KSH + H_2O.$$

Evaporated *in vacuo* it crystallizes in colorless rhombohedra, of the formula $2KSH + H_2O$, which deliquesce in the air. At 200°, it loses its water of crystallization, and at a higher temperature fuses to a yellowish liquid, which solidifies to a reddish mass. Like the hydroxide, it has an alkaline reaction. On adding an equivalent quantity of potassium hydroxide to the sulphydrate solution, we get potassium sulphide:

$$KSH + KOH = K_2S + H_2O.$$

Potassium Sulphide, K_2S, is usually obtained as a porous mass by gently heating a mixture of potassium sulphate and carbon in well-closed crucibles:

$$K_2SO_4 + 2C = K_2S + 2CO_2.$$

When fused, it solidifies to a red crystalline mass. It crystallizes from concentrated aqueous solutions with five molecules of water, in colorless prisms, which deliquesce in the air. The solution absorbs oxygen from the air, and is decomposed into potassium hyposulphite and caustic potash:

$$2K_2S + H_2O + 2O_2 = K_2S_2O_3 + 2KOH.$$

Potassium hydrosulphide and sulphide precipitate insoluble sulphides from the solutions of many metallic salts. They are decomposed by acids with liberation of hydrogen sulphide.

When the aqueous solution of the sulphide is boiled with sulphur the *polysulphides*, K_2S_3, K_2S_4, and K_2S_5, are formed. The aqueous solutions of the polysulphides are decomposed by acids, with disengagement of hydrogen sulphide and separation of sulphur (milk of sulphur). The so-called *liver of sulphur* (*Hepar sulphuris*, *K. sulphuratum*), a liver-brown mass, used in medicine, is obtained by the fusion of potassium carbonate with sulphur, and consists of a mixture of potassium trisulphide with potassium sulphate and hyposulphite.

The aqueous solution of the potassium, as well as that of the sodium sulphide, dissolves some metallic sulphides, and forms sulpho-salts with them (pp. 223, 225).

When dry ammonia is conducted over heated potassium, potassamide (NH_2K) results. This is a dark-blue liquid which solidifies to a white, crystalline mass. It sublimes at about 400°, and above that temperature breaks down into its elements. Water decomposes it into potassium hydroxide and ammonia.

Recognition of the Potassium Compounds.—In all of its compounds potassium is present as a positive univalent element. Almost all of the potassium compounds are easily soluble in water. The few exceptions serve for the characterization and separation of potassium. Tartaric acid added to the solution of a potassium salt gives a crystalline precipitate of acid potassium tartrate. Platinic chloride ($PtCl_4$) produces in potassium solutions a yellow, crystalline precipitate of $PtCl_4 . 2KCl$ (p. 271). Potassium silicofluoride, K_2SiFl_6, is also sparingly soluble and can be used in detecting and estimating potassium. Potassium compounds introduced into the flame of an alcohol or a gas lamp impart to the same a *violet* coloration. The spectrum of the flame is characterized by two bright lines, one red and one violet (see Spectrum Analysis).

2. RUBIDIUM AND CÆSIUM.

Rb = 85.4. Cs = 133.

Rubidium and cæsium are the perfect analogues of potassium (p. 273). They were discovered by means of the spectroscope, by Bunsen and Kirchhoff, in 1860. Although only occurring in small quantities, they are yet very widely distributed, and frequently accompany potassium in mineral springs, salt, and plant ashes. The mineral lepidolite contains 0.5 per cent. of rubidium; upward of 30 per cent. of cæsium oxide is present in the very rare pollucite, a silicate of aluminium and cæsium. Stassfurt carnallite also contains rubidium. The spectrum of rubidium is marked by two red and two violet lines; cæsium by two distinct blue lines; hence the names of these elements (*rubidus*, dark red; *cæsius*, sky-blue).

Rubidium and cæsium form double chlorides ($PtCl_4 . 2RbCl$, $PtCl_4 . CsCl$) with platinum chloride, and they are more insoluble than the double platinum salt of potassium, hence may answer for the separation of these elements from potassium. This is also true of the compounds $2RbCl . SnCl_4$, $2CsCl . SnCl_4$ and $2SbCl_3 . 3CsCl$, which are rather sparingly soluble.

Rubidium and cæsium may be obtained free by decomposing the fused chloride with the electric current. Erdmann and Köthner [Ann. Ch. **294** (1897), 58] obtained large yields of rubidium by heating its hydroxide with magnesium in a seamless, knee-shaped iron tube:

$$2RbOH + 2Mg = 2Rb + 2MgO + H_2.$$

Dry hydrogen is conducted through the tube while heating. The rubidium, which distils over, is collected under liquid paraffin. Metallic rubidium has a silver-white color, with a somewhat yellowish tinge; its vapor is greenish-blue. Its specific gravity equals 1.52; its melting point is 38.5°. Oxygen at the ordinary temperature converts it into *rubidium dioxide*, RbO_2, consisting of dark-brown crystals, which are transposed by water at a gentle heat into oxygen and rubidium hydroxide:

$$2RbO_2 + 2H_2 = 2RbOH + H_2O + O.$$

The dioxide dissolves in water with hissing and the tumultuous evolution of oxygen; hydrogen peroxide is produced at the same time. The oxide RbO is not known. The *iodide* at present is quite frequently substituted in medicine for potassium iodide.

Cæsium like rubidium is isolated by heating cæsium hydroxide with magnesium powder in an atmosphere of hydrogen or by the electrolysis of a mixture of cæsium and barium cyanides. Electrodes of aluminium are employed for this purpose. Cæsium is a silver-white metal, of specific gravity 1.85. It oxidizes quite readily and inflames in the air. It melts at 26.5° and boils at 270°.

Since 1892 Wells and Wheeler, and also Erdmann, have prepared an interesting series of cæsium and rubidium halides. The metals in these appear to be trivalent and also quinquivalent, *e. g.*, $RbClBr_2$, $RbBr_3$, $RbCl_4I$, $CsBr_3$, $CsBr_3I_2$, CsI_5. Rubidium iodine tetrachloride, $RbICl_4$, results in conducting chlorine into a rubidium iodide solution. It crystallizes in monoclinic yellow leaflets. It dissolves with difficulty in water. Its solution acts as a powerful oxidant; it dissolves gold and platinum. It is still undetermined whether these are atomic or only double compounds (*e. g.*, $RbCl . ICl_3$). The rubidium and cæsium compounds are distinguished from those of potassium by entering into union more readily and in greater proportion with other halides to form double salts, *e. g.*, with $AsCl_3$, $AsBr_3$ and AsI_3, with which potassium double halides have not been prepared.

3. SODIUM.

Na = 23.05.

Sodium is widely distributed in nature, especially as chloride in sea-water and as rock-salt; and is also found in silicates. Its nitrate is Chili saltpeter, and its fluoride in union with aluminium fluoride constitutes the cryolite of Greenland. The metal was obtained in 1807, by Davy, by the action of a strong electric current upon fused sodium hydroxide. It was formerly (1855), like potassium, obtained upon a large scale by igniting a mixture of sodium carbonate, finely divided anthracite and limestone in an iron retort:

$$Na_2CO_3 + 2C = 2Na + 3CO.$$

A great advance was made in its manufacture when Castner (1866), at Oldbury, Birmingham, reduced the hydrate instead of the carbonate with carbon impregnated with finely divided, spongy iron. Gay-Lussac and Thénard (1808) had reduced the hydroxide with metallic iron at a white heat:

$$2NaOH + 2Fe = 2Na + 2FeO + H_2.$$

Netto (1898, Wallsend, Newcastle-on-Tyne) invented a most satisfactory process, abandoning it, however, later. It consisted in allowing molten caustic soda to run over wood charcoal placed in vertical iron retorts. Sodium vapors escaped constantly from an exit tube at the top, while fused carbonate ran out from a tube at the bottom:

$$3NaOH + C = Na_2CO_3 + Na + H_3.$$

The sodium vapors were condensed in flat iron receivers and the liquid metal was collected under rock oil.

Castner and Kellner electrolyzed a salt solution, using mercury as anode; the amalgam was then distilled when mercury was expelled and sodium remained.

Grabau electrolyzed fused salt after reducing its melting point by adding potassium and strontium chlorides. The sodium then escaped in vapor form.

Sodium can be made on a small scale by heating the peroxide with freshly ignited wood charcoal:

$$3Na_2O_2 + 2C = Na_2 + 2Na_2CO_3.$$

Calcium carbide may be substituted for the charcoal:

$$7Na_2O_2 + 2CaC_2 = 2CaO + 4Na_2CO_3 + 3Na_2.$$

The action in both cases is very energetic.

Sodium in external properties is very similar to potassium. It melts at 95.6°, boils at 742°, and is converted into a colorless vapor, which burns with a bright yellow flame in the air. It oxidizes readily on exposure, and decomposes water even in the cold, although less energetically than potassium. A piece of sodium thrown upon water swims about upon the surface with a rotary movement, the disengaged hydrogen, however, not igniting. If we prevent the motion, by confining the metal to one place, the heat liberated by the reaction attains the ignition temperature of hydrogen, and a flame follows, as was also observed with potassium (p. 40).

Sodium Oxide, Na_2O, is not definitely known.

Sodium Peroxide, Na_2O_2, has recently been introduced into commerce as a bleaching agent. It is made by heating sodium in a stream of dry air, using vessels of aluminium and a temperature below 300°. It is a yellow-white powder. It melts with greater difficulty than caustic soda, and at elevated temperatures gives off oxygen. Water decomposes it with caustic soda and oxygen which escapes upon boiling. With ice-water it forms a solution containing both caustic soda and hydrogen peroxide. On careful evaporation such solutions yield crystalline hydrates of sodium superoxide. Anhydrous acids and alcohol appear to decompose it with the formation of a peculiar hydrate:

$$Na_2O_2 + HCl = NaCl + NaO_2H,$$

which probably has the formula Na-O-O-H. Sodium superoxide acts on many organic compounds with the production of flame and the separation of carbon. At a red heat it is superior to all other oxidants in its powerful action (1 part of the material, 2 parts of soda and 4 parts of sodium superoxide).

Sodium Hydroxide, sodium hydrate, or caustic soda, NaOH, like potassium hydroxide, is formed by boiling a solution of sodium carbonate with calcium hydroxide:

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH.$$

At present it is directly produced in the soda manufacture by adding a little more carbon to the fusion (see Soda); or by the electrolysis of sodium chloride (pp. 290, 291).

The sodium hydroxide which solidifies after fusion is a white, radiating, crystalline mass, and resembles caustic potash very much. It attracts water from the air, becomes moist, and coats itself by carbon dioxide absorption with a white layer of sodium carbonate (caustic potash deliquesces perfectly, because the resulting carbonate is also deliquescent). The aqueous solution, called sodium hydroxide, resembles that of potassium. Crystals of $NaOH + 3\frac{1}{2}H_2O$ separate at 0° from the concentrated solution; they melt at 6°.

Sodium Chloride, NaCl, is abundant in nature. It is found almost everywhere in the earth and in natural waters; in sea-water it averages 2.7–3.2 per cent. As rock-salt it forms large deposits in many districts, especially at Stassfurt and Wieliczka in Galicia (p. 276).

In warm climates, on the coasts of the Mediterranean Sea, sodium chloride is gotten from the sea according to the following procedure: At high tide sea-water is allowed to flow into wide, flat basins (salt gardens), in which it evaporates under the sun's heat; the working is limited, therefore, to summer time. After sufficient concentration, pure sodium chloride first separates, and this is collected by itself. Later, there crystallizes a mixture of sodium chloride and magnesium sulphate; finally potassium chloride, magnesium chloride and some other salts appear (among them potassium iodide and bromide), the separation of which constitutes a special industrial branch in some regions. In cold climates, as in Norway and at the White Sea, the cold of winter is employed for the production of salt. In the freezing of sea-water, as well as of other solutions, almost pure ice separates at first; the enriched sodium chloride solution is then concentrated in the usual way.

Rock-salt is either mined in shafts, or, where the strata are not so large and are admixed with other varieties of rock, a lixiviation process is employed. Borings are made in the earth and water runs into them, or into any openings already formed. When the water has saturated itself with sodium chloride, it is pumped to the surface and the brine then further worked. In many regions, especially in Reichenhall, in Bavaria, more or less saturated natural salt or brine springs flow from the earth. The concentration of the non-saturated brine occurs at first in the so-called "graduation" houses. These are long wooden frames filled with fagots, and on letting the salt water run upon them it will be distributed and evaporated by the fall; the concentrated brine collects in the basin below, and is then evaporated over a free fire.

Sodium chloride crystallizes from water in transparent cubes, of specific gravity 2.13, which arrange themselves by slow cooling into hollow, four-sided pyramids. It melts at 815° and volatilizes at a white heat. It is not much more soluble in hot than in cold water; 100 parts at 0° dissolve 36 parts of salt; at 100°, 39 parts. The saturated solution, therefore, contains about 26 per cent. of sodium chloride. If the saturated solution be cooled below —10, large monoclinic tables ($NaCl + 2H_2O$) separate; these lose water at 0° and become cubes.

The ordinary sodium chloride usually contains a slight admixture of magnesium salts, in consequence of which it gradually deliquesces in the air; the perfectly pure salt is not hygroscopic. When heated the crystals crackle, because of the escape of the mechanically enclosed water.

Sodium Bromide and **Iodide** crystallize at ordinary temperatures with two molecules of water, which they lose again at 30°; above 30° they separate in anhydrous cubes. Sodium bromide fuses at 760° and the iodide at 690°; the former is difficultly soluble in alcohol and the latter is very soluble.

Sodium Chlorate ($NaClO_3$) and **Perchlorate** ($NaClO_4$) are considerably more soluble in water than the corresponding potassium salts.

Sodium Iodate, $NaIO_3$, is obtained in the same manner as the potassium salt, and at ordinary temperatures crystallizes with three molecules of water in silky needles. It is present in Chili saltpeter. If chlorine gas be conducted through the warmed solution of sodium iodate in sodium hydroxide, the periodate $IO\left\{\begin{matrix}(ONa)_2\\(OH)_3\end{matrix}\right.$ (see p. 181) crystallizes out on cooling. This becomes the normal salt ($NaIO_4 + 3H_2O$) when dissolved in nitric acid.

Sodium Sulphate (*Natrium sulphuricum*), Na_2SO_4, crystallizes at ordinary temperatures with ten molecules of water of crystallization, and is then known as Glauber's salt (*Sal mirabile Glauberi*). It occurs in many mineral waters, and in large deposits, with or without water of crystallization, in Spain. It is a by-product in the manufacture of sodium chloride from sea-water and brine. It is produced in large quantities by heating salt with sulphuric acid:

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl,$$

and is used in making soda (sodium carbonate). Or it may be prepared by the method of Hargreaves, by conducting sulphur dioxide, air and steam over strongly ignited sodium chloride:

$$2NaCl + SO_2 + O + H_2O = Na_2SO_4 + 2HCl.$$

More recently the sulphate has been obtained by a transposition of sodium chloride with magnesium sulphate at a winter temperature—a procedure which is prosecuted chiefly in Stassfurt, where immense quantities of magnesium sulphate (kieserite) exist:

$$2NaCl + MgSO_4 = MgCl_2 + Na_2SO_4.$$

Sodium sulphate crystallizes at ordinary temperatures with ten molecules of water, in large, colorless, monoclinic prisms, which crumble in the air and fall into a white powder. The salt $Na_2SO_4 + 10H_2O$ is only stable at temperatures below 34°. It melts at 34°, separating into a saturated solution and the anhydrous salt Na_2SO_4. The latter melts at about 886°.

This explains the remarkable alteration which the solubility of Glauber's salt sustains in water at 34°. As a rule the solubility of a substance in water does not change suddenly with the temperature, but gradually. A sudden change in solubility is connected with a change in condition of the substance passing into solution. This applies also to Glauber's salt. 100 parts of water dissolve, at 0°, 12 parts; at 18°, 48 parts; at 25°, 100 parts; at 30°, 200 parts; at 34°, 354 parts of the hydrous salt. At the last temperature the solubility is greatest; by further increase of heat it gradually diminishes; at 50°, 100 parts of water dissolve only 263 parts; at 100°, 238 parts of the salt. This is explained by the fact that up to 34° the solubility relates to the salt $Na_2SO_4 + 10H_2O$, which cannot exist at higher temperatures. From this point upwards the solubility relates to the anhydrous salt which separates as a deposit in small rhombic pyramids, if the solution of the hydrous salt, saturated at 34°, be heated higher.

When the solution, saturated at 34°, is allowed to cool to the ordinary temperature, and even lower, not the slightest separation of crystals occurs, although the salt is vastly more insoluble at lower temperatures than at 34°. Many other salts form *supersaturated solutions*, although they are less striking than that of Glauber's salt. The supersaturated solution of the latter may be agitated and twirled about without crystallization setting in. If, however, a glass rod, or some other solid body, be introduced into the solution, it will solidify suddenly to a crystalline mass. The particles of dust floating about in the air will have a like effect; therefore, to preserve the supersaturated solution, the vessel containing it should be kept well corked. By accurately made investigations, it has been determined that the crystallization of the supersaturated Glauber's salt solution is only induced by contact with already formed crystals. These must then be present everywhere in the atmosphere, because only solids that have been exposed to the air, and that have not been carefully cleansed afterward, bring about the crystallization.

In the crystallization of a supersaturated Glauber's salt solution considerable heat is disengaged, and the mass increases in temperature. This is because the latent heat of all substances in the liquid condition is greater than in the solid. At 10°, occasionally, and of their own accord, transparent crystals, $Na_2SO_4 + 7H_2O$, separate from the supersaturated solutions. These crystals change readily to anhydrous sodium sulphate and Glauber's salt.

This salt is employed in medicine as a purgative, and finds extended application in the manufacture of glass and in the preparation of soda.

The **primary** or **acid sodium sulphate**, $NaHSO_4$, is obtained by the action of sulphuric acid upon the neutral salt or upon sodium chloride:

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

At ordinary temperatures it crystallizes with one molecule of water, and is perfectly analogous to the potassium salt.

The sodium salts of sulphurous acid are obtained by conducting sulphur dioxide into solutions of sodium hydroxide or carbonate. The *secondary sulphite*, Na_2SO_3, crystallizes with seven molecules of water at ordinary temperatures; in the presence of sodium hydroxide, or by warming the solution, it separates in the anhydrous state. The *primary sulphite*, $NaHSO_3$, consisting of small, easily soluble crystals, gives up sulphur dioxide in the air, and is oxidized to sodium sulphate. According to Schwicker, when it is neutralized with potassium carbonate it forms yellow, indistinct crystals of **sodium potassium sulphite**, $NaKSO_3 + H_2O$. Primary potassium sulphite on the other hand, when neutralized with soda, yields the salt $NaKSO_3 + 2H_2O$, consisting of hard, yellowish crystals. This forms entirely different compounds with organic iodides from those which the first salt (with which it is isomeric, if the water of crystallization be disregarded) affords. Two isomeric sodium potassium hyposulphites, $NaKS_2O_3$, are obtained when these salts take up sulphur. The following formulas express their structure:

$$K\text{–}SO_2\text{–}ONa \qquad Na\text{–}SO_2\text{–}OK$$
$$KS\text{–}SO_2\text{–}ONa \qquad NaS\text{–}SO_2\text{–}OK.$$

[Ber. **22** (1889), 1728; see also pp. 186, 198.]

Sodium Hyposulphite, $Na_2S_2O_3$, **Sodium Thiosulphate,** is prepared by boiling the aqueous solution of neutral sodium sulphite with flowers of sulphur:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

It is obtained as a by-product in the recovery of sulphur from the soda residues. It crystallizes with five molecules of water, in large monoclinic prisms, dissolves very readily in water, and is somewhat deliquescent in the air. At 56° it melts in its water of crystallization; loses all water at 100°, and decomposes by further heating into sodium sulphate and sodium pentasulphide, Na_2S_5. When the dry salt is heated in the air, the sulphur of the polysulphide burns with a blue flame. Acids decompose the aqueous solution with separation of sulphur and evolution of sulphur dioxide (p. 197):

$$Na_2S_2O_3 + 2HCl = 2NaCl + SO_2 + S + H_2O.$$

Like the sulphate, it readily affords supersaturated solutions. The hyposulphite is used as a reducing agent; chlorine, bromine and iodine are converted by it into the corresponding halogen salts. An iodine solution is instantaneously decolorized by sodium hyposulphite with the production of sodium tetrathionate (p. 199). Chlorine behaves differently; sulphuric acid and sodium chloride are produced. Upon this reaction rests the application of sodium hyposulphite as an *antichlor* in chlorine bleaching, to remove the excess of the chlorine, which has a destructive action upon the fiber. In consequence of its property of dissolving the halogen silver derivatives, it is employed in photography.

Sodium Carbonate (Soda), Na_2CO_3. This, technically, very important salt is obtained (1) as natural soda, (2) from the ashes of plants, and (3) by chemical methods.

1. *Natural soda* disintegrates from the soil in certain districts, as in Hungary, Asia, and Africa, during the hot seasons. It is a constituent of many mineral springs, *e. g.*, Carlsbad, and of the soda seas of Egypt, of Central Africa, and of the coasts of the Caspian and Black Seas, of California, and of German East Africa. In these seas or lakes a salt deposits having the formula

$$Na_2CO_3 + NaHCO_3 + 2H_2O.$$

In Egypt it is called *tro-na* and in Colombia *urao.* Its occurrence at Owen's Lake, Inyo County, California, is the only one of scientific importance. The waters of this lake upon evaporation yield very large quantities of quite pure soda.

2. *Soda from the Ashes of Plants.*—Before Le Blanc's process came into use the greater portion of soda was made from the ashes of sea and coast plants (*Chenopodium*, *Salsola*, *Atriplex*, *Salicornia*, etc.); these assimilate the sodium salts of the earth, while the land plants absorb the potassium salts, and for this reason contain potashes in their ash. In Southern France and in Spain beach plants were and are yet specially cultivated for this purpose. The Spanish soda was particularly rich in

carbonate and controlled the markets for a long period. At present soda from the ashes of plants possesses only a local interest.

3. In the *chemical way* soda is prepared almost exclusively from salt (NaCl). The following methods are in use: (1) That discovered in 1794 by Le Blanc; (2) the ammonia-soda process introduced in 1866, and (3) the *electrolytic method* of recent date. To these may be added the (4) cryolite soda process.

1. In the Le Blanc method the sodium chloride is converted into sodium sulphate by warming with sulphuric acid (pp. 58, 287). When the latter is dry, it is mixed with charcoal and chalk (calcium carbonate) and ignited in a reverberatory furnace. Two principal phases may be distinguished in this reaction. First, the carbon reduces the sodium sulphate to sodium sulphide:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

The sodium sulphide then acts upon the calcium carbonate to form calcium sulphide and sodium carbonate:

$$Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

At the same time the high temperature converts a portion of the calcium carbonate into calcium oxide and carbon dioxide, which is reduced by the ignited carbon to the monoxide:

$$CaCO_3 = CaO + CO_2; \quad CO_2 + C = 2CO.$$

The appearance of the latter, which burns with a bluish flame, indicates the end of the action. The chief products in the soda fusion are, then, sodium carbonate and calcium sulphide, mixed with varying amounts of calcium carbonate, calcium oxide, and foreign substances. This fused mass is called *crude soda*. It is lixiviated in specially constructed apparatus with cold water; the sodium carbonate dissolves, and there remain behind calcium sulphide, calcium carbonate, and a portion of the foreign substance—the *soda residue*.

During the lixiviation the caustic lime present in the crude soda acts upon the sodium carbonate with the assistance of water, and there result calcium carbonate and sodium hydrate. The latter passes into solution with the soda:

$$CaO + H_2O + Na_2CO_3 = CaCO_3 + 2NaOH.$$

It is possible by the Le Blanc process to obtain a preponderance of sodium hydroxide if the soda fusion be mixed at the beginning with more carbon, heated intensely and the crude soda be then extracted with hot water.

When the solution is evaporated the soda will separate from the hot liquid as a crystalline powder, $Na_2CO_3 + H_2O$. It is removed from the liquid, and new liquors are introduced, etc. The mother liquor, the so-called red liquor, contains finally caustic soda and sodium sulphide almost exclusively. The soda flour is freed from the mother liquor by a centrifugal, dried and calcined—*calcined soda*. For further purification it is recrystallized from water, when it separates in large, transparent crystals of the formula $Na_2CO_3 + 10H_2O$—*crystallized soda.*

The by-products and the refuse in the manufacture of soda—hydrochloric acid and soda residues—must be utilized as fully as possible, because of the enormous competition encountered by the manufacturers. To this end the hydrochloric acid is converted by the process described on page 50, into chlorine and bleaching lime and the soda residues are worked in various ways to get their sulphur content into an available form. Of late years the Chance-Claus method has been adopted. It consists in decomposing the residues with carbonic acid: $CaS + H_2O + CO_2 = CaCO_3 + H_2S$, and burning the liberated hydrogen sulphide either with an insufficiency of air, when sulphur will separate: $H_2S + O = H_2O + S$, or with an excess of air when sulphur dioxide is formed: $H_2S + 3O = H_2O + SO_2$. The last product is then conducted into lead chambers (p. 189). About 70,000 tons of sulphur are recovered annually (regenerated sulphur).

2. The *ammonia-soda process* is based upon the transposition of sodium chloride with primary ammonium carbonate to ammonium chloride and primary sodium carbonate:

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl.$$

This change takes place at the ordinary temperature. The acid sodium carbonate being sparingly soluble in cold water, is converted into sodium carbonate upon ignition:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The ammonium chloride remains in solution. Ammonia is recovered from it by means of lime. In actual practice carbon dioxide is conducted under pressure into a concentrated salt solution saturated with ammonia:

$$NaCl + NH_3 + CO_2 + H_2O = NH_4Cl + NaHCO_3.$$

The temperature must not exceed 40°. The carbonic acid is obtained by burning lime, and when the bicarbonate is heated half of it is recovered. The lime from the calcite is used to generate ammonia from ammonium chloride. The raw material in this process consists therefore of salt and limestone which, with the assistance of ammonium salts, are converted into soda and calcium chloride (p. 50).*

This process is exceedingly simple from the chemical standpoint. Difficulties arose in building the necessary apparatus on a technical scale and they militated against the general adoption of the method. Fortunately they have been completely overcome, and this is due in a large measure to E. Solvay, so that at present the production of soda by the Le Blanc process is becoming less frequent. It is only in England that the old method holds sway.

3. The Le Blanc method with its improvements was in operation for a century before it was displaced by the ammonia-soda process, and now the latter is being seriously threatened by a dangerous rival—the electrolytic production of caustic alkalies, alkaline carbonates, chlorine and potassium chlorate (p. 275). When an aqueous salt solution is electrolyzed chlorine separates at the anode and sodium at the kathode. The latter acts

---

* Magnesite and magnesia can be substituted for limestone and lime.

immediately on the water, producing hydrogen and sodium hydroxide. The free chlorine would produce sodium chloride and hypochlorite or chlorate (pp. 175, 176) if the kathode and anode liquors were not separated by a porous diaphragm. Difficulties, in the constructing of the diaphragms, confronted the technical utilization of the process. There is no substance which does not gradually disintegrate when used as anode. However, all these objectionable features have been, in a measure, overcome. The sodium hydroxide is obtained as such or it is separated in the form of the sparingly soluble bicarbonate upon conducting carbonic acid through its solution. The chlorine is brought into trade in the liquid form or it is changed to bleaching lime.

4. Considerable quantities of soda are obtained at present from cryolite, a compound of aluminium fluoride and sodium fluoride ($AlFl_3 . 3NaFl$), which occurs in great deposits in Greenland. The pulverized mineral is ignited with burned lime or chalk; insoluble calcium fluoride and a very soluble compound of aluminium oxide with sodium oxide, called sodium aluminate (see Aluminium), are produced:

$$2(AlFl_3 . 3NaFl) + 6CaO = 6CaFl_2 + Al_2O_3 . 3Na_2O.$$

The mass is treated with water and carbon dioxide, obtained by burning lime, conducted into the solution, which causes the precipitation of aluminium oxide, and sodium carbonate dissolves:

$$Al_2O_3 . 3Na_2O + 3H_2O + 3CO_2 = Al_2(OH)_6 + 3Na_2CO_3.$$

This method is no longer in use in Europe. It continues of value in North America and in Denmark, because these countries control large deposits of cryolite. Calcium fluoride is largely employed by them in the manufacture of glass and porcelain; the aluminium oxide is used for making alum, aluminium sulphate or metal.

At ordinary temperatures sodium carbonate crystallizes with ten molecules of water ($Na_2CO_3 + 10H_2O$) in large monoclinic prisms, which crumble upon exposure and become a white powder. It melts at 50° in its water of crystallization, and upon heating a pulverulent hydrate, $Na_2CO_3 + 2H_2O$, separates, which in dry air has one molecule of water, and at 100° loses all of this. At 30–50° rhombic prisms of the composition $Na_2CO_3 + 7H_2O$, crystallize from the aqueous solution. The anhydrous salt absorbs water from the air but does not deliquesce. It melts at 850° and volatilizes somewhat at a very high temperature. 100 parts of water dissolve 7 parts at 0°, and at 38°, 52 parts of the anhydrous salt. At more elevated temperatures the solubility is less, as in the case of the sulphate. Sodium carbonate has a strong alkaline reaction; acids liberate carbon dioxide from it.

Primary Sodium Carbonate, ordinary bicarbonate of soda (*Natrium bicarbonicum*), $NaHCO_3$, is produced by the action of carbon dioxide upon the hydrous secondary carbonate:

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3.$$

It crystallizes without water, in small monoclinic tables; it dissolves, however, at ordinary temperatures in 10–11 parts of water, and possesses feeble alkaline reaction. By heating and by boiling the solution it passes into the secondary carbonate with disengagement of carbon dioxide. The dry salt decomposes rapidly even below 100°. By rapid evaporation small monoclinic prisms of the so-called sodium sesquicarbonate, $Na_2CO_3 + 2NaHCO_3 + 2H_2O$, separate. The salt which deposits in the sodium seas of Hungary and Egypt, has the composition $Na_2CO_3 + NaHCO_3 + 2H_2O$ (p. 289).

Sodium Nitrate, $NaNO_3$, Chili saltpeter, is found in immense deposits in Peru. The saltpeter earth contains of sodium nitrate from 15 to 65 parts out of 100 parts, the rest being sodium chloride, a little potassium nitrate, potassium perchlorate and sodium iodate (pp. 55, 178). The soil is extracted with boiling water; on cooling, crude saltpeter separates; it is purified by recrystallization. It crystallizes in rhombohedra very similar to cubes, hence designated *cubic saltpeter*, to distinguish it from the "*prismatic*" potassium saltpeter. It fuses at about 318°. In water it is somewhat more easily soluble than potassium saltpeter. In the air it attracts moisture, hence it is not adapted for the manufacture of gunpowder. In other respects it is perfectly similar to potassium nitrate. It is largely used in the manufacture of nitric acid, and especially in preparing potassium saltpeter (p. 279).

Sodium Nitrite, $NaNO_2$, is prepared like potassium nitrite (p. 280), by heating sodium nitrate with lead, iron, or graphite. It crystallizes more readily than potassium nitrite, and does not deliquesce in the air. It occurs in trade in small colorless crystals, containing from 93 to 98 per cent. of the pure salt. It is largely used in the dye industry for the preparation of the azo-compounds.

Sodium Phosphates.—The sodium salts of phosphoric acid are less soluble and crystallize better than those of potassium. The *trisodium phosphate*, Na_3PO_4, is made by saturating one molecule of phosphoric acid with three molecules of sodium hydroxide, and crystallizes in six-sided prisms with twelve molecules of water. It has a strong alkaline reaction, absorbs carbon dioxide from the air, and is converted into the secondary salt.

Disodium phosphate, Na_2HPO_4, is the most stable of the sodium phosphates, and hence is generally employed in laboratories (*Natrium phosphoricum*). It may be obtained by saturating phosphoric acid with sodium hydroxide to feeble alkaline reaction, or may be prepared on a large scale by decomposing bone ashes (tricalcium phosphate) with an equivalent amount of sulphuric acid and precipitating the calcium as dicalcium phosphate with soda. It crystallizes at ordinary temperatures with twelve molecules of water in large monoclinic prisms which effloresce rapidly in the air. It separates from solutions with a temperature above 30° in non-efflorescing crystals containing seven molecules of water. It is soluble in 4–5 parts of water, and shows a feeble alkaline reaction. When heated the salt loses water, melts at about 300° and becomes *sodium pyrophosphate*, $Na_4P_2O_7$, which crystallizes with ten molecules of water, and upon boiling with nitric acid passes into primary sodium phosphate.

The *primary* or *monosodium phosphate*, NaH_2PO_4, crystallizes with one molecule of water, and exhibits a faintly acid reaction. At 100° it loses its water of crystallization, and at 200° becomes *disodium pyrophosphate*, $Na_2H_2P_2O_7$, which at 240° forms *sodium metaphosphate*, $NaPO_3$:

$$Na_2H_2P_2O_7 = 2NaPO_3 + H_2O.$$

We get various modifications of the metaphosphate, according to the conditions of fusing and cooling; they are probably polymerides, corresponding to the formulas $Na_2P_2O_6$, $Na_3P_3O_9$, etc. Upon heating sodium metaphosphate with metallic oxides the latter dissolve, and salts of orthophosphoric acid are formed, *e. g.*:

$$NaPO_3 + CuO = CuNaPO_4.$$

In this manner, characteristic colored glasses (phosphorus beads) are obtained with various metals. In blowpipe analysis this behavior serves for the detection of the respective metals.

The salts of *arsenic acid* are perfectly analogous to those of phosphoric acid. Of the antimoniates may be mentioned the disodium pyroantimoniate, $Na_2H_2Sb_2O_7 + 6H_2O$, which is insoluble in cold water, and is therefore precipitated from the soluble sodium salts on the addition of dipotassium-pyroantimoniate.

The phosphates show more plainly than the sulphates that the hydrogen atoms of a polyhydric acid, replaceable by metals, are not of equal importance for the "strength" of the acid. The hydrogen first replaced acts like the hydrogen of a strong acid, while the second and third follow it successively. This is also seen in the reactions of the aqueous solutions and may be explained by the theory of electrolytic dissociation as follows: The dissociation of phosphoric acid into the ions PO_4H_2' and H' is that of an acid of medium strength (p. 269). The second hydrogen atom is dissociated like a feeble acid and the third is not at all dissociated in aqueous solution. Consequently the solution of sodium triphosphate does not contain the trivalent anion PO_4''' together with the sodium ions. As the third hydrogen atom of the acid shows less tendency to dissociate than water the following transposition immediately takes place: $PO_4''' + \underbrace{H' + HO'} = PO_4H'' + HO'$, so that the solution contains the ions $PO_4H'' — 2Na'$ and $Na' — OH'$, which are the cause of its alkaline reaction.

Sodium Borate.—The normal salts of boric acid, $B(OH)_3$, and metaboric acid, $BO.OH$ (see p. 242), are not very stable. The ordinary alkaline borates are derived from tetraboric acid ($H_2B_4O_7$), which results from the condensation of four molecules of the normal boric acid:

$$4B(OH)_3 - 5H_2O = H_2B_4O_7.$$

The most important of the salts is *borax*, which crystallizes at ordinary temperatures with ten molecules of water in large monoclinic prisms, $Na_2B_4O_7 + 10H_2O$. Borax occurs naturally in some lakes of Thibet, whence it was formerly imported under the name of *tinkal*. At present, it is prepared artificially by boiling or fusing boric acid with sodium carbonate. At ordinary temperatures, the crystals dissolve in 14 parts of water, at 100° in one-half part; the solution has a feeble alkaline reaction. When heated to 70° rhombohedra crystallize from the concentrated solution, and have the composition $Na_2B_4O_7 + 5H_2O$, formerly known as *octahedral borax*. Both salts puff up when heated, lose water, and yield a white, porous mass (*burned borax*), which fuses at 880° to a transparent vitreous mass ($Na_2B_4O_7$). In fusion this dissolves many metallic oxides, forming transparent glasses (*borax beads*), which frequently possess characteristic colors; thus copper salts give a blue and chromic oxide gives a green glass. Therefore, borax may be employed in blowpipe tests for the detection of certain metals. Upon this property of dissolving metallic oxides depends the application of borax for the fusion and soldering of metals.

Sodium Silicate (sodium water-glass) is analogous to the potassium salt, and is most readily obtained by fusing quartz with sodium sulphate and charcoal.

The sulphur compounds of sodium are also analogous to those of potassium.

Sodium Nitride, NaN_3 (sodium azoimide), is the sodium salt of hydrazoic acid, N_3H. It results from derivatives of azoimide, by neutralizing the free acid or by decomposing the ammonium salt with caustic soda. W. Wislicenus prepared it by heating sodamide (p. 283) to 150–250° in a current of nitrous oxide:

$$NaNH_2 + N_2O = NaN_3 + H_2O.$$

The water produced here decomposes a portion of sodamide into sodium hydroxide and ammonia:

$$NaNH_2 + H_2O = NaOH + NH_3$$

[Ber. 25 (1892), 2084; see also Z. f. anorg. Ch. 6 (1894), 38]. It can be recrystallized from water or may be precipitated by alcohol from water. Its solution reacts alkaline and has a very salty taste. It is not exploded by a blow, but this occurs when it is heated. [Curtius, Ber. 24 (1891), 3346; see also p. 133.]

Recognition of Sodium Compounds.—Almost all the sodium salts are easily soluble in water, sodium pyroantimoniate, $Na_2H_2Sb_2O_7$, excepted; this is precipitated from solutions of sodium salts by potassium pyroantimoniate, and can serve for the detection of sodium. Sodium compounds, exposed in a colorless flame, impart to the latter an intense yellow. The spectrum of the sodium flame is characterized by a very bright yellow line, which, when more strongly magnified, splits into two lines. (See Spectrum Analysis.)

4. LITHIUM.

$Li = 7.03.$

Lithium occurs in nature only in small quantities, but is tolerably widely disseminated, and is found in some mineral springs and in the ashes of many plants, notably in that of tobacco and the beet. As a compound silicate, it occurs in lepidolite or lithia mica; as phosphate (with iron and manganese) in triphylite, and (with aluminium, sodium, and fluorine) in amblygonite.

The metal is separated from the chloride, or, better, from the more easily fusible mixture of equal parts of lithium chloride and potassium chloride, by means of the electric current, and is silver-white in color, decomposing water at ordinary temperatures. Its specific gravity is 0.59. It is the lightest of all the metals, and swims upon naphtha. It melts at 180°, and burns with an intense light. It burns energetically in hydrogen at a red heat to *lithium hydride*, LiH, which is a comparatively stable white powder. The lithium salts are at present prepared almost entirely from amblygonite; they are very similar to the salts of sodium, but closely approach those of magnesium.

Lithium Chloride, LiCl, crystallizes, at ordinary temperatures, in anhydrous, regular octahedra; below 10°, however, it has two molecules of water, and deliquesces in the air.

Lithium Phosphate, $Li_3PO_4 + \frac{1}{2}H_2O$, and **Lithium Carbonate,** Li_2CO_3. are difficultly soluble in water; therefore they are precipitated from solutions of lithium salts by sodium phosphate or carbonate. By strong ignition the carbonate loses carbon dioxide. So far as these two salts and also lithium fluoride, which is soluble in very little water, are concerned, lithium approaches the metals of the second group (p. 273). Its compounds color the flame a beautiful red; the spectrum shows an intense red line together with a faint yellow line.

AMMONIUM COMPOUNDS.

Upon p. 128 we observed that ammonia combines directly with the acids to form salt-like compounds, which are analogous to the metallic salts, especially those of potassium with which they are isomorphous. The univalent group, NH_4, playing the rôle of metal in these derivatives, is called *ammonium*, and the derivatives of ammonia, *ammonium compounds*. The metallic character of the group NH_4 is confirmed by the existence of *ammonium amalgam*, which, as regards its external appearance, is very similar to the sodium and potassium amalgams. Ammonium amalgam may be prepared by letting the electric current act upon ammonium chloride, NH_4Cl, viz., by immersing the negative platinum electrode into a depression in the ammonium chloride, which is filled with mercury and stands upon the positive electrode. Then, as in the case of the decomposition of potassium or sodium chloride, the metallic ion—ammonium—separates on the negative pole, and combines to an amalgam with mercury. The amalgam may also be obtained if sodium amalgam be covered with a concentrated solution of ammonium chloride:

$$\underset{\text{Sodium amalgam.}}{(Hg + Na)} \text{ and } NH_4Cl \text{ yield } \underset{\text{Ammonium amalgam.}}{(Hg + NH_4)} \text{ and } NaCl.$$

Ammonium amalgam forms a very voluminous mass with a metallic appearance. It is very unstable, and decomposes rapidly into mercury, ammonia and hydrogen.

The aqueous solution of ammonia reacts strongly alkaline, and from its entire behavior we must assume the existence of ammonium hydroxide (NH_4OH) in the solution. This is justified because there are many organic derivatives of ammonium hydroxide, in which the hydrogen of the ammonium is replaced by hydrocarbon residues; *e. g.*, tetramethyl ammonium hydroxide, $N(CH_3)_4OH$. These are thick liquids, of strong basic reaction and, in all respects, are very similar to potassium and sodium hydroxides.

Ammonium Chloride, NH_4Cl (*Sal ammoniacum*), is sometimes found in volcanic districts, and was formerly obtained by the dry distillation of camel's dung (p. 126). At present it is prepared almost exclusively from the ammonia water of gas works. This water contains ammonium sesquicarbonate in addition to the other ammonium salts. It is distilled with lime and the escaping ammonia caught in hydrochloric or sulphuric acid. The ammonium chloride is carefully heated and recrystallized or sublimed. By sublimation it is obtained as a compact, fibrous mass. It dissolves in 2.7 parts of cold and in one part of boiling water, and crystallizes from the solution in small, feather-like, grouped octahedra or cubes, of sharp, salty taste. When heated, ammonium chloride sublimes without melting; at the same time a dissociation into ammonia and hydrochloric acid is sustained, but these products recombine to ammonium chloride on cooling. The dissociation begins at 280° and is complete at 350°, and the vapor density corresponds to that of a mixture of similar molecules, of NH_3 and HCl, *i. e.*, $\frac{17.07 + 36.46}{2} = 26.76$ ($O_2 = 32$). A like decomposition is sustained by the ammonium chloride when its solution is boiled; ammonia escapes and the solution contains some free hydrochloric acid.

Ammonium Sulphate, $(NH_4)_2SO_4$, crystallizes without water in rhombic prisms, and is soluble in two parts of cold and one part of hot water. It fuses at 140°, and by further heating decomposes. Most of it is used as a fertilizer.

Ammonium Persulphate (pp. 188, 279), $(NH_4)_2S_2O_8$, obtained by the electrolysis of ammonium sulphate, is at present made on a large scale and is used as an oxidant. It consists of very soluble monoclinic crystals. It decomposes when its aqueous solution is evaporated, yielding ammonium sulphate, free sulphuric acid and oxygen. This salt is applied in making the other persulphates.

Ammonium Nitrate, NH_4NO_3, is isomorphous with potassium nitrate and deliquesces in the air. It melts at 159°; at 170° decomposition into nitrous oxide and water commences and is tumultuous at 240° (p. 211). It has been recently applied in the manufacture of blasting material.

Ammonium Nitrite, NH_4NO_2, is present in minute quantities in the air, and results from the action of the electric spark upon the latter when moist. It may be obtained by the saturation of aqueous ammonia with nitrous acid [Z. f. anorg. Ch. 7 (1894), 34], and in a perfectly pure condition by the decomposition of silver or lead nitrite by ammonium chloride. Heat decomposes it, especially when in concentrated solution, into nitrogen and water (p. 115).

The decomposition of ammonium nitrite into water and nitrogen and ammonium nitrate into nitrous oxide and water are both exothermic reactions, occurring with the disengagement of heat and are independent of the pressure of the disengaged gas; the components do not reunite to form their original compounds. This is not a case of dissociation (p. 274).

Ammonium Hyponitrite, $NH_4\text{-}O\text{-}N{=}N\text{-}O\text{-}NH_4$, has been prepared recently by conducting ammonia into an ethereal solution of hyponitrous acid. It forms white crystals. It melts at 64° with violent decomposition. It gradually breaks down at the ordinary temperature into ammonia, water and nitrous oxide [see p. 212 and Hantzsch and Kaufmann, Ann. Chem. 292 (1896), 317].

Ammonium Carbonate.—The *neutral* or *secondary* salt $(NH_4)_2CO_3$, separates as a crystalline powder, when ammonia gas is conducted through a concentrated solution of commercial ammonium carbonate. It parts with ammonia in the air and becomes the *primary* or *acid* salt, NH_4HCO_3, which, when heated to 58°, dissociates into carbon dioxide, ammonia, and water.

The common commercial, so-called *sesquicarbonate of ammonium*, is generally a mixture of primary ammonium carbonate with ammonium carbamate $(NH_4)HCO_3 + NH_2CO_2 . NH_4$. The latter may be obtained by the direct union of carbon dioxide with ammonia; water immediately converts it into the neutral salt (p. 234). Experience has demonstrated that the commercial salt quite often contains carbon dioxide and ammonia in the same proportion as the acid salt, $(NH_4)HCO_3$. It arises in the decay of many nitrogenous carbon compounds, *e. g.*, the urine, and was formerly prepared by the dry distillation of bones, horn, and other animal substances. At present it is obtained by heating a mixture of ammonium chloride, or sulphate, with calcium carbonate. It then sublimes as a white, transparent, hard mass.

Primary Ammonium Carbonate, NH_4HCO_3, is obtained by saturating ammonium hydroxide with carbon dioxide. It is a white, odorless powder, rather insoluble in water. In aqueous solution it gradually loses carbon dioxide and is changed to the secondary carbonate.

Ammonium Phosphates.—The most important of these is the *secondary ammonium-sodium phosphate*, $NH_4NaHPO_4 + 4H_2O$, ordinarily termed *salt of phosphorus* (*Sal microcosmicum*). It is found in guano and in decaying urine. It can be obtained by the crystallization of a mixture of disodium phosphate and ammonium chloride:

$$Na_2HPO_4 + NH_4Cl = NH_4NaHPO_4 + NaCl.$$

It consists of large, transparent, monoclinic crystals. When heated it fuses, giving up water and ammonia and forms a transparent glass of sodium metaphosphate, $NaPO_3$ (p. 294). It serves in blowpipe tests for the detection of various metals.

The *tertiary ammonium phosphate*, $(NH_4)_3PO_4$, separates, in crystalline form, upon mixing concentrated solutions of phosphoric acid and ammonia. Upon drying, it loses ammonia and passes into the *secondary salt*, $(NH_4)_2HPO_4$, which changes to the *primary salt*, $(NH_4)H_2PO_4$, when its solution is boiled. This is in harmony with what was said on p. 294 relative to the behavior of phosphoric acid.

Ammonium Nitride, $N_3(NH_4)$, the ammonium salt of hydrazoic acid, obtained from an organic body, diazohippuramide, or by saturating hydrazoic acid with ammonia, is precipitated from its alcoholic solution by ether in the form of a snow-white, crystalline powder. It separates from alcohol in compact, colorless leaflets, consisting of step-like groups of crystals. It resembles ammonium chloride in this respect. It crystallizes from water in large, transparent prisms, which soon become opaque. It has a slight alkaline reaction; it is not hygroscopic; it dissolves readily in water and in alcohol. It is exceedingly volatile; it gradually disappears in the air and it is also carried off by aqueous and alcoholic vapors. It sublimes, when gently heated, in small, shining prisms; on rapid heating it explodes (Curtius, p. 132).

Ammonium Sulphide, $(NH_4)_2S$, results upon mixing 1 volume of hydrogen sulphide with 2 volumes of ammonia at —18°. It is a white crystalline mass, dissociating, at ordinary temperatures, into NH_4SH and NH_3. In aqueous solution it also seems to dissociate into its constituents. At 45° it completely dissociates into ammonia and hydrogen sulphide:

$$(NH_4)_2S = \underset{\text{2 vols.}}{2NH_3} + \underset{\text{1 vol.}}{H_2S}.$$

Ammonium Hydrosulphide, NH_4SH, is produced upon conducting hydrogen sulphide into an alcoholic ammonia solution. It is completely dissociated at 45°:

$$NH_4SH = \underset{\text{1 vol.}}{NH_3} + \underset{\text{1 vol.}}{H_2S}.$$

It is obtained in aqueous solution by saturating aqueous ammonia with hydrogen sulphide. At first the solution is colorless, but on standing in contact with the air becomes yellow, owing to the formation of ammonium polysulphides, $(NH_4)_2S_n$. The so-called yellow ammonium sulphide is more easily obtained by the solution of sulphur in the colorless hydrosulphide. Both solutions are often employed in laboratories for analytical purposes.

Recognition of Ammonium Compounds.—All ammonium salts are volatile or decompose upon heating. The alkalies and other bases liberate ammonia from them, which is recognized by its odor and the blue color it imparts to red litmus-paper. Platinum chloride produces a yellow crystalline precipitate of ammonio-platinum chloride, $PtCl_4 . 2NH_4Cl$, in solutions of ammonium chloride. An excess of tartaric acid precipitates primary ammonium tartrate.

METALS OF THE SECOND GROUP.

		Ca 40		Sr 87.6		Ba 137.4	
Be 9.1	Mg 24.36						
			Zn 65.4		Cd 112		Hg 200.3.

The second group of the periodic system (see Table, p 246) comprises chiefly the bivalent metals, which form compounds of the type MeX_2, and in their entire deportment exhibit many analogies. Their special relations and analogies are more closely regulated by their position in the periodic system. Beryllium and magnesium belong to the two small periods whose members are similar but do not show complete analogy. Beryllium exhibits many variations from magnesium, and in many properties approaches aluminium; just as lithium attaches itself to magnesium (p. 273).

The metals calcium, strontium, and barium constitute the second members of the three great periods, are very similar to one another (p. 244), and in accord with their strong basic character, attach themselves to the alkali metals—potassium, rubidium and cæsium. Zinc, cadmium, and mercury, which correspond to them and constitute the second sub-group, really belong to the right, negative sides of the three great periods. They fall in with the heavy metals, are much less basic, and resemble the alkaline earth metals only in their combination types. In consequence of the double periodicity of the three great periods both sub-groups (Ca, Sr, Ba and Zn, Cd, Hg) exhibit many analogies to magnesium and beryllium.

I. GROUP OF THE ALKALINE EARTHS.

Calcium, . . Ca = 40 Strontium, . . Sr = 87.6 Barium, . . Ba = 137.4.

The metals of this group are termed alkaline earth metals, because their oxides attach themselves in their properties, on the one side to the oxides of the alkalies, upon the other to the real earths (alumina, etc.). Their atomic weights bear almost the same ratio to one another as those of the alkali metals, hence the alkaline earth metals show the same gradation in properties as the elements of the potassium group. With increase in atomic weight and atomic volume, their chemical energy and basicity become greater. Barium decomposes water energetically, and oxidizes more readily than strontium and calcium. In accord with this, we find barium hydroxide a stronger base; it dissolves rather readily in water, does not decompose upon ignition, and absorbs carbon dioxide rapidly from the air. Barium carbonate is also very stable, fuses at a white heat, and only disengages a little carbon dioxide. Calcium hydroxide, on the other hand, dissolves with more difficulty in water, and when ignited, breaks down into water and calcium oxide; the carbonate also yields carbon dioxide when similarly treated. In its entire character, strontium stands between barium and calcium. All these affinity relations find full expression in the heat of formation of the corresponding compounds (p. 327).

While the alkaline earth metals are similar to the alkalies in their free condition and in their hydroxides, they differ essentially from them by the insolubility of their carbonates and phosphates, and still more of their sulphates. Barium sulphate is only soluble to the slightest degree in water and acids, while strontium sulphate is about 40 times and calcium sulphate about 800 times as soluble (p. 309).

The atomic weights of these metals have been determined in part from their specific heats, but mainly from their isomorphism with the metals of the magnesium group (pp. 253, 255).

1. CALCIUM.

Ca = 40.

Calcium belongs to the class of elements most widely distributed upon the earth's surface. As calcium carbonate (limestone, marble, chalk) and the sulphate (gypsum, alabaster), it represents immense deposits in all stratified formations. As phosphate, it constitutes *phosphorite*, as fluoride, *fluorite*, both of which are abundant. As silicate, it is found in most of the oldest crystalline rocks.

The metal is obtained, according to Moissan, by heating calcium iodide with an excess of sodium to a dark-red heat. The liberated metal dissolves in the sodium, and when cold the latter is removed by anhydrous alcohol. It dissolves with the evolution of hydrogen to sodium alcoholate. The calcium remains as a brilliant white crystalline powder. It can also be prepared by the electrolysis of the fused chloride or iodide. Although the affinity of calcium for oxygen is less than that of the alkalies, yet the oxide (also barium oxide and strontium oxide) cannot be reduced to metal by ignition with carbon, iron, or sodium—due, probably to the non-fusibility of the oxide. These oxides, however, are reduced in the electric furnace; the liberated metals combine at once with carbon to yield metallic carbides (pp. 253, 307).

Calcium is a yellow, shining metal, of specific gravity 1.55–1.6. In dry air it is tolerably stable, in moist it is covered with a layer of hydroxide. It decomposes water with considerable energy. It fuses at a red heat, and in the air burns with a brilliant yellow light. If the metal be heated in nitrogen to a red heat *calcium nitride*, Ca_3N_2, results. This is a brown mass which water decomposes with the formation of calcium hydrate and ammonia. Lithium, strontium, barium and magnesium behave similarly (p. 316). Calcium slowly unites with hydrogen at the ordinary temperature, but rapidly at a red heat, forming *calcium hydride*, CaH_2, an earthy, gray powder, which decomposes water more energetically than calcium itself.

Calcium Oxide, CaO (lime), may be obtained pure by igniting the nitrate or carbonate. It is prepared on a large scale by burning the ordinary limestone or marble ($CaCO_3$) in lime-kilns. It is a grayish-white amorphous mass, which becomes crystalline at 2500° and liquid like water at 3000°. It vaporizes at higher temperatures (Moissan). The oxyhydrogen flame thrown upon a piece of lime causes it to emit an extremely intense white light (Drummond's lime light). In the air lime attracts moisture and carbon dioxide, becoming calcium carbonate; burned lime unites with water with evolution of much heat, breaking down into a white voluminous powder of calcium hydroxide, $Ca(OH)_2$—*slaked lime*.

When limestone contains large quantities of alumina, magnesium carbonate, or other constituents, the lime from it slakes with difficulty, and is known as *poor* lime, to distinguish it from pure *fat* or *rich* lime, which is readily converted into a powder of hydroxide with water.

Calcium Hydroxide, $Ca(OH)_2$ (slaked lime), is a white, porous powder which dissolves with difficulty in cold water (1 part in 760 parts), but with still more difficulty in warm water; the solution saturated in the cold (lime-water) becomes cloudy upon warming. It has a strong alkaline reaction. *Milk of lime* is slaked lime mixed with water. In the air it attracts carbon dioxide and forms calcium carbonate. At a red heat it decomposes into oxide and water.

Slaked lime is employed in the preparation of ordinary mortar, a mixture of calcium hydroxide, water and sand. The hardening of the mortar in the air depends mainly upon the fact that the calcium hydroxide combines with the carbon dioxide of the air to form the carbonate, and at the same time acts upon the silicic acid of the sand forming a calcium silicate, which, in time, imparts durability to the mortar.

Hydraulic mortar, or *cement*, is produced by gently igniting a mixture of limestone or chalk with aluminium silicate (clay) and quartz powder. On stirring the powdered, burnt mass with water it soon hardens, and is then not affected by water. Some naturally occurring limestones, containing upwards of 20 per cent. of clay, yield hydraulic cements, without any admixtures after burning. Their composition varies, and also the process of their hardening; the latter, however, depends principally upon the formation of calcium and aluminium silicates.

Calcium Peroxide, CaO_2, is precipitated as a hydrate in crystalline leaflets, if lime-water be added to a solution of hydrogen peroxide. It contains eight molecules of water, which it gradually loses in dry air.

The halogen derivatives of calcium, like those of other metals, are prepared by the solution of the oxide or carbonate in the aqueous haloid acids. They are formed also by the direct union of calcium with the halogens; this occurs with evolution of flame. Technically, calcium chloride is often obtained as a by-product, *e. g.*, in the preparation of ammonia (see Soda).

Calcium Chloride, $CaCl_2$, crystallizes from aqueous solution with six molecules of water, in large, transparent, six-sided prisms, which deliquesce in the air. *In vacuo* it loses four molecules of water. When heated, it melts in its water of crystallization, loses water, but it is only after it has been exposed above 200° that it becomes anhydrous; then it is a white, porous mass. The dry salt melts at 806°, and solidifies on cooling to a crystalline mass, which attracts water energetically, and may be employed in the drying of gases and liquids. The dry calcium chloride also absorbs ammonia, forming the compound $CaCl_2 . 8NH_3$. The crystallized hydrous salt dissolves in water with reduction of temperature; by mixing with snow or ice the temperature is lowered to —48°. Upon fusing the dry chloride in moist air it will partly decompose into the oxide and hydrogen chloride.

Calcium bromide and iodide are very similar to the chloride.

Calcium Fluoride, $CaFl_2$, occurs in nature as *fluorite*, in large cubes or octahedra, or even in compact masses. It is often discolored by impurities. It is found, in sparing quantities, in the ashes of plants, bones, and the enamel of the teeth. A soluble fluoride added to the solution of calcium chloride throws down insoluble calcium fluoride as a white voluminous precipitate. If, however, the calcium chloride solution be poured into a boiling dilute solution of potassium fluoride, the calcium fluoride is obtained in little transparent crystals.

The fluoride is perfectly insoluble in water, and is only decomposed by strong acids. It fuses easily at a red heat, serving, therefore, as a flux in the smelting of ores. When heated it phosphoresces.

Calcium Hypochlorite, $Ca(ClO)_2$, is not known in a pure condition. The so-called *bleaching lime* or *chloride of lime*, obtained by conducting chlorine, at ordinary temperatures, over slaked lime, contains calcium hypochlorite as the active principle.

According to analogy to the action of chlorine upon potassium or sodium hydroxide (p. 278), the reaction in the case of calcium hydroxide may be expressed by the following equation:

$$2Ca(OH)_2 + 2Cl_2 = Ca(ClO)_2 + CaCl_2 + 2H_2O.$$

This would incline us to regard chloride of lime as a mixture of calcium hypochlorite, calcium chloride, and water. In accordance with the equation, the completely chlorinated chloride of lime must contain 48.9 per cent. of chlorine, which is never the case, because a portion of the calcium hydroxide invariably remains unaltered. Calcium chloride does not exist free in bleaching lime, because it is not withdrawn from the latter by alcohol, and nearly all the chlorine of the bleaching lime can be expelled by carbon dioxide. It is therefore probable that the compound, $Ca{<}^{Cl}_{OCl} = CaCl_2O$ (Odling and Lunge), is present in bleaching lime; its formation, then, from calcium hydroxide would correspond to that of the chloride and hypochlorite from the caustic alkalies:

$$\begin{matrix} NaOH \\ NaOH \end{matrix} + Cl_2 = \begin{matrix} NaCl \\ NaOCl \end{matrix} + H_2O,$$

$$Ca\left\{\begin{matrix} OH \\ OH \end{matrix}\right. + Cl_2 = Ca\left\{\begin{matrix} Cl \\ OCl \end{matrix}\right. + H_2O.$$

Chloride of lime is a white, porous powder with an odor resembling that of chlorine. The aqueous solution has a strong alkaline reaction, and bleaches. It decomposes in the air as the carbon dioxide of the latter liberates hypochlorous acid. Even in closed vessels it gradually decomposes with the evolution of oxygen; the decomposition is hastened by sunlight and heat, and may occur with explosion. Hence chloride of lime should be preserved in loosely closed vessels, in a cool, dark place.

Dilute hydrochloric or sulphuric acid will expel chlorine from chloride of lime; the quantity liberated is just twice that which the hypochlorite eventually found in it contains (p. 175):

$$CaCl(OCl) + 2HCl = CaCl_2 + H_2O + Cl_2.$$

By the action of sulphuric acid all the chlorine of the bleaching powder is liberated, whereby calcium chloride first yields hydrochloric acid:

$$CaCl(OCl) + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

The application of chloride of lime for the production of chlorine in chlorine bleaching and disinfection is based on this deportment.

The quantity of chlorine set free by acids from the chloride of lime represents its quantity of so-called *active chlorine;* good chloride of lime should contain at least 25 per cent.

When a small quantity of cobaltic oxide or a cobalt salt is added to the solution of bleaching lime, and heat applied, a regular stream of oxygen is disengaged; this is an advantageous method of preparing oxygen. Other oxides, like those of manganese, copper, and iron, behave similarly. In this reaction there occurs, apparently, a catalytic action of the oxides. The reaction is explained, doubtless, in the same way as the action of hydrogen peroxide upon certain oxides (see pp. 88, 102).

On warming bleaching lime with ammonia, the following decomposition occurs:

$$3CaCl(OCl) + 2NH_3 = 3CaCl_2 + 3H_2O + N_2.$$

This reaction can be used for the preparation of nitrogen.

Calcium Sulphate, $CaSO_4$, is very abundant in nature. In an anhydrous condition it forms the mineral *anhydrite,* crystallizing in forms of the rhombic system. With two molecules of water it occurs as gypsum, in large monoclinic crystals or in granular, crystalline masses (alabaster, etc.). It also separates as a fine crystalline powder, $CaSO_4 + 2H_2O$, when soluble calcium salts are precipitated with sulphuric acid. Calcium sulphate dissolves with difficulty in water; 1 part at average temperatures is soluble in 400 parts of water. When heated to 110° gypsum loses all its water, and becomes *burnt* gypsum; when this is pulverized and mixed with water, it forms a paste which hardens to a solid mass in a short time. The hardening is dependent upon the reunion of anhydrous calcium sulphate with two molecules of water. On this depends the use of burned gypsum for the production of casts, figures, etc. In case gypsum is heated above 160° (dead-burnt gypsum), it will no longer harden with water; the naturally occurring anhydrite behaves in the same manner.

Calcium Nitrate, $Ca(NO_3)_2$, is produced by the decay of the nitrogenous organic substances in the presence of lime, therefore, it is frequently found as an efflorescence upon walls (in cattle stables). It crystallizes from water in monoclinic prisms, containing four molecules of water; the anhydrous salt deliquesces in the air and is easily soluble in alcohol. By the action of potassium carbonate or chloride, calcium nitrate can be transposed into potassium nitrate (p. 280).

Calcium Phosphates.—The *tertiary* phosphate, $Ca_3(PO_4)_2$, is found in slight quantities in most of the mountain rocks. In combination with calcium chloride and fluoride, it crystallizes as *apatite.* As phosphorite, it forms compact masses, more or less intimately mixed with other constituents, and occurs in immense deposits in Spain, France, Germany, Russia and Florida. When these minerals disintegrate the calcium phosphate passes into the soil and is absorbed by the plants. In the latter, it accumulates chiefly in the seeds and grains. In the animal kingdom, it is principally found in the bones, the ashes of which contain upwards of 82 per cent. of tricalcium phosphate. Tertiary calcium phosphate is nearly insoluble in water. If disodium phosphate be added to the aqueous solution of a calcium salt, and then ammonium hydroxide, it will separate as a gelatinous precipitate, which, after drying, becomes a white amorphous powder. It is very readily soluble in acids, even acetic.

The *secondary* calcium phosphate, $CaHPO_4 + 2H_2O$, is sometimes present in guano, in the form of small, shining prisms; it separates as an amorphous precipitate, if disodium phosphate be added to a solution of calcium chloride mixed with some acetic acid. When ignited, it passes into pyrophosphate, $Ca_2P_2O_7$ (p. 216).

The *primary* phosphate, $Ca(H_2PO_4)_2$, is produced by the action of sulphuric or hydrochloric acid upon the first two phosphates. It is readily soluble in water. It changes to metaphosphate when it is heated:

$$Ca(H_2PO_4)_2 = Ca(PO_3)_2 + 2H_2O.$$

Calcium phosphate is present in all plants. Its presence in the soil is, therefore, an indispensable condition for its fertility. When there is a scarcity of phosphoric acid it must be added. To this end, bone meal and pulverized phosphorite were formerly employed. Since, however, the phosphoric acid is contained in these substances as tricalcium phosphate, which is not easily absorbed by the plants, the primary phosphate is extensively employed at present as a fertilizer, or, better, the mixture resulting from the action of sulphuric acid upon the tertiary salt, which also contains calcium sulphate. Superphosphate is the name applied to the resulting mass.

The Thomas slag, obtained in the dephosphorization of iron ores by the Gilchrist-Thomas process, constitutes a very valuable and important crude product from which to prepare calcium phosphate. It also contains a crystallized phosphate of the formula $Ca_4P_2O_9$, which may be regarded as a derivative of the normal hydrate, $P(OH)_5$:

$$2P(OH)_5 - H_2O = H_8P_2O_9.$$

Calcium Carbonate, $CaCO_3$, is very widely distributed in nature. It crystallizes in two crystallographic systems, hence is dimorphous. In rhombic crystals, with the specific gravity 3.0, it forms aragonite. In hexagonal rhombohedra, with the specific gravity 2.7, it occurs as calcite. Iceland spar, employed for optical purposes, is perfectly pure, transparent calcite. The common calcite, which constitutes immense mountain chains, is an amorphous or indistinctly crystalline stratum, and is usually mixed with other constituents, as clay. When the limestone is granular and crystalline, it is termed marble. Dolomite also forms large layers, and is a compound or amorphous mixture of calcium and magnesium carbonates, with generally an excess of the former. *Chalk* is very pure amorphous calcium carbonate, consisting of the shells of microscopic sea animals. Calcium carbonate is, further, a regular constituent of all plants and animals; the shells of eggs, of mussels, even corals and pearls, consist chiefly of it.

A soluble carbonate, added to the aqueous solution of a calcium salt, precipitates calcium carbonate as a white, amorphous powder, which soon becomes crystalline. In the cold, it assumes the form of calcite; upon boiling the liquid, it generally changes into aragonite crystals. Magnesite ($MgCO_3$), siderite ($FeCO_3$), smithsonite ($ZnCO_3$) and rhodochrosite ($MnCO_3$) are isomorphous with calcite, while witherite ($BaCO_3$), strontianite ($SrCO_3$) and cerussite ($PbCO_3$) are isomorphous with aragonite.

Calcium carbonate is almost insoluble in pure water; but dissolves somewhat in water containing carbon dioxide, as it very probably is changed to the *primary* carbonate, $Ca(HCO_3)_2$. One thousand parts of water at 15° and medium barometric pressure dissolve about 0.385 part of primary calcium carbonate [Z. f. anorg. Ch. 17 (1898) 170]. For this reason, we find calcium bicarbonate dissolved in all natural waters. When the solution stands exposed, or if it be heated, carbon dioxide escapes, and the secondary carbonate again separates out. The formation of lime scales, thermal tufts, stalactites, boiler scales and similar deposits are due to this. Calcium carbonate, like all carbonates, is decomposed by acids, with evolution of carbon dioxide.

At a red heat, it dissociates into calcium oxide and carbon dioxide. The change begins at 600°. The tension of dissociation (p. 274) is 85 mm. at 860°, and at 1040° 510–520 mm. For this reason calcium carbonate is not decomposed when heated in a sealed tube.

Calcium Silicate, $CaSiO_3$, occurs as white, crystalline wollastonite. It is also a constituent of most natural silicates and of the artificial silicate fusion—glass.

Glass.—The silicates of potassium and sodium are readily fusible and soluble in water. The silicates of calcium and the other alkaline earths are insoluble, very difficultly fusible, and generally crystallize when they cool. If, however, the two silicates be fused together, an amorphous, transparent mass, of average fusibility, results; it is only slightly attacked by water and acids—it is glass. To prepare the latter, a mixture of sand, lime, and soda, or potash, is heated to fusion in a muffle furnace. Instead of the carbonates of potassium and sodium a mixture of the sulphates with charcoal can be employed; the carbon reduces the sulphates to sulphides, which form silicates when fused with silicon dioxide.

Glass, depending on its constituents, arranges itself into two classes:

1. Lime glass (free from lead).
2. Lead glass.

1. The lime glass consists either of sodium-lime (soda glass) or potassium-lime (potash glass).

Soda glass—a mixture of sodium and calcium silicates—fuses readily, and is employed for window-panes and ordinary glass vessels. *Potash* or *Bohemian glass*, also called crown glass, consists of calcium and potassium silicates, is not very fusible, is harder and withstands the action of water and acids better than soda glass; it is, therefore, employed in the manufacture of chemical glassware.

The best lime glass, *normal glass*, is a trisilicate corresponding to the formula

$$K_2O \text{ (or } Na_2O) + CaO + 6SiO_2.$$

2. Lead glass is constituted like lime glass, containing, however, lead oxide for calcium oxide.

Glass crystal or *flint glass* is composed of potassium and lead silicates. It is not as hard, fuses with tolerable readiness, refracts light strongly, and when polished, acquires a clear luster. On this account it is employed for optical purposes (for lenses, prisms) and is used in ornamental glassware. *Strass*, a lead glass containing boron trioxide, is used to imitate precious stones. The opaque varieties of enamel consist of lead glass and in the fused glass are insoluble admixtures, as tin dioxide and calcium phosphate.

Ordinary window or bottle glass is obtained by the fusion of rather impure materials; in consequence of the presence of ferrous oxide it is ordinarily colored green. To remove this coloration, manganese peroxide, MnO_2, is added to the fusion. It oxidizes a portion of the ferrous to ferric oxide, the silicate of which is colored slightly yellow, while manganese forms a violet silicate. These colors, violet and green, almost neutralize each other as complementaries. The colored glasses contain silicates of colored metallic oxides: chromic and cupric oxides color green; cobaltic oxide, blue; cuprous oxide, a ruby red, etc.

The sulphur compounds of calcium are very much like those of the alkalies. **Calcium**

Sulphide, CaS, is most readily obtained by heating the sulphate with carbon, and is a whitish-yellow mass. It melts in the electric furnace and crystallizes on cooling. When it is dissolved in water we get **Calcium Hydrosulphide**, $Ca(SH)_2$ (in addition to calcium hydroxide), which decomposes on boiling the aqueous solution. When calcium oxide is ignited with sulphur in a closed crucible a yellowish-gray mass is obtained, which consists of calcium polysulphides and sulphate. Milk of lime boiled with sulphur yields a deep-yellow solution of calcium polysulphides and calcium hyposulphite. When these solutions are acted upon by acids, finely divided sulphur—milk of sulphur—is precipitated and hydrogen sulphide set free. If the reverse occur, viz., the addition of a solution of polysulphides to an excess of dilute acids, hydrogen persulphide will separate (p. 110).

Calcium Carbide, CaC_2. Its importance in illumination has been dwelt upon on pp. 154, 155. Fr. Wöhler (1862) first described it. He obtained it by heating intensely an alloy of zinc and calcium with carbon:

$$ZnCa + C_2 = CaC_2 + Zn.$$

W. Borchers was the first person to prepare it in the electric furnace. In 1891 he emphasized the fact, after years of experience, that all oxides could be reduced by carbon heated electrically. Wilson made carbide accidentally on a large scale in 1892. Moissan followed shortly after. Both chemists obtained the carbide in crystals. It may be procured pure in shining gold-like, non-transparent crystals, if burnt marble is heated electrically with sugar carbon:

$$CaO + 3C = CaC_2 + CO.$$

Its specific gravity is 2.2. It resists most of the strongly reacting substances, yet water and dilute acids decompose it energetically with liberation of acetylene (p. 154). At present it is made in many factories from unslaked lime and coal or coke (see the publication of Liebetanz, p. 155). Strontium and barium carbides are similar to calcium carbide.

2. STRONTIUM.

Sr = 87.6.

This element is rather rare in nature, and is principally found in strontianite (strontium carbonate) and celestite (strontium sulphate). Its compounds are very similar to those of calcium.

The metal is obtained by the electrolysis of fused strontium chloride. It has a brass-yellow color, and a specific gravity of 2.5. It oxidizes in the air and burns with a bright light when heated. It decomposes water at the ordinary temperature.

Of the compounds of strontium we may mention the following:

Strontium Oxide, SrO, is most readily obtained by igniting the nitrate. It unites with water, with strong evolution of heat, forming

Strontium Hydroxide, $Sr(OH)_2$, which is more readily soluble in water than calcium hydroxide. It crystallizes from aqueous solution with eight or nine molecules of water. When ignited it decomposes into strontium oxide and water, but with more difficulty than calcium hydroxide.

Strontium Chloride, $SrCl_2 + 6H_2O$, crystallizes from water in hexagonal tables, which deliquesce in the air; it is easily soluble in alcohol.

Strontium Sulphate, $SrSO_4$, is much more difficultly soluble in water than calcium sulphate, but is not as insoluble as barium sulphate [one liter dissolves 107 mg. at 15°].

Strontium Nitrate, $Sr(NO_3)_2$, is obtained by dissolving the carbonate in nitric acid, and is readily soluble in water, but insoluble in alcohol. It crystallizes from warm solutions in anhydrous octahedra, but from cold, with four molecules of water, in monoclinic prisms. Mixed with combustible substances it colors the flame a beautiful carmine-red, and for this reason is employed in pyrotechny.

Strontium Carbonate, $SrCO_3$, is precipitated from aqueous solutions of strontium salts by soluble carbonates, as an amorphous, insoluble powder. When ignited (1100°) it breaks down into strontium oxide and carbon dioxide. This decomposition does not, however, occur as easily as with calcium carbonate.

3. BARIUM.

Ba = 137.4.

Barium occurs in nature in large masses, as heavy spar (or barium sulphate), and as witherite (barium carbonate). All its compounds are distinguished by their high specific gravity, hence the name barium, from βαρὺς, heavy. In accordance with its general character, barium is a stronger basic metal than either strontium or calcium (p. 299).

The barium salts are either prepared from the natural witherite, by dissolving it in acids, or from heavy spar. The technical procedure consists in heating barium sulphate with carbon and calcium chloride when barium chloride and potassium sulphide (in addition to carbon monoxide) are formed:

$$BaSO_4 + 4C + CaCl_2 = BaCl_2 + CaS + 4CO.$$

Metallic barium, like strontium and calcium, was first obtained (Humphry Davy, 1808) by electrolysis. Bunsen used the fused chloride for this purpose. The following method is more convenient: Sodium amalgam is added to a hot saturated barium chloride solution; the sodium displaces the barium, which forms an amalgam with the mercury. The resulting liquid barium amalgam is kneaded with water, to remove all the sodium, and then heated in a stream of hydrogen, to volatilize the mercury.

Barium is a bright yellow metal, of specific gravity 3.6. It fuses at a red heat, but vaporizes with difficulty. It is rapidly oxidized in the air; like sodium it decomposes water very energetically, even at the ordinary temperature.

Barium Oxide, BaO, is obtained by the ignition of barium nitrate. It is a gray, amorphous mass, of specific gravity 5.5, and is fusible in the oxyhydrogen flame. With water it yields the hydroxide, with evolution of much heat.

Barium Hydroxide, $Ba(OH)_2$, is precipated from concentrated solutions of barium salts by potassium or sodium hydroxide, not, however, by ammonium hydroxide. It is obtained on a large scale by igniting heavy spar with carbon, when barium sulphide is formed, and its aqueous solution desulphurized with zinc oxide:

$$BaS + ZnO + H_2O = ZnS + Ba(OH)_2;$$

also upon heating barium carbonate together with carbon in a current of steam:

$$BaCO_3 + C + H_2O = Ba(OH)_2 + 2CO.$$

At the ordinary temperature it dissolves in 20 parts of water; upon boiling, in 3 parts. From aqueous solution it crystallizes with eight molecules of water in four-sided prisms or leaflets. The solution—called *baryta water*—is strongly alkaline and is very similar to the alkalies. When exposed to the air it absorbs carbon dioxide and becomes turbid, with separation of barium carbonate. At a red heat it fuses, like the caustic alkalies, without decomposition, and on cooling solidifies to a crystalline mass.

Barium Peroxide, BaO_2, is produced when barium oxide (ignited barium nitrate) is heated in a current of dry air (free from carbonic acid) or oxygen; it always contains barium oxide. To purify it, the commercial peroxide is rubbed together with water and added to cold, very dilute hydrochloric acid, until the latter is almost saturated. An excess of baryta water is added to the solution, containing barium chloride and hydrogen peroxide, when *hydrated barium peroxide,* $BaO_2 + 8H_2O$, separates in shining scales, which, upon warming, readily lose water and break down into a white powder consisting of barium peroxide. The latter is a compact gray mass when obtained directly from the oxide.

The peroxide dissolves in dilute acids, with production of hydrogen peroxide. Concentrated sulphuric acid sets free ozonized oxygen from it. When strongly ignited (at about 700°) it decomposes into barium oxide and oxygen. See p. 81 for its use in the technical production of oxygen. It is also employed for bleaching purposes and for the preparation of hydrogen peroxide; see pp. 99, 100.

Barium Chloride, $BaCl_2$, crystallizes from aqueous solution, with two molecules of water, in large, rhombic tables, which are stable in the air. It dissolves readily in water, and is poisonous, like all soluble barium salts.

Barium Nitrate, $Ba(NO_3)_2$, crystallizes in anhydrous, shining octahedra, of the regular system, soluble in 12 parts of cold and 3 parts of hot water. Technically it is made by mixing concentrated solutions of barium chloride with sodium nitrate, when barium nitrate is precipitated. It is employed as a green fire in pyrotechny.

Barium Sulphate, $BaSO_4$, is found in nature as heavy spar, in rhombic prisms, with a specific gravity of 4.6. It is obtained artificially by the precipitation of barium salts with sulphuric acid, in the form of a white, amorphous powder, almost insoluble in water and acids. Under the name of *permanent white,* it is used as a paint, as a substitute for poisonous *white lead,* from which it is also distinguished by its unalterability.

Barium Persulphate, BaS_2O_8 (pp. 188, 198), obtained by rubbing the ammonium salt together with barium hydroxide, crystallizes from its solution (*in vacuo*) in prisms, containing four molecules of water of crystallization. It soon decomposes, yielding barium sulphate, sulphuric acid, and oxygen:

$$BaS_2O_8 + H_2O = BaSO_4 + H_2SO_4 + O.$$

Barium Carbonate, $BaCO_3$, as witherite, occurs in shining, rhombic crystals, and is precipitated from barium solutions by soluble carbonates, as a white, amorphous powder. It fuses at a white heat, and loses carbon dioxide at 1400–1500°.

Barium Sulphide, BaS, is obtained by igniting the sulphate with carbon. It dissolves in water, with decomposition into hydroxide and hydrosulphide.

RECOGNITION OF THE COMPOUNDS OF THE ALKALINE EARTHS.

The carbonates and phosphates of this group are insoluble in water; hence are precipitated from the aqueous solutions of their salts upon the addition of soluble carbonates and phosphates (of the alkalies). The sulphates are also sparingly soluble in acids; for this reason they are thrown down from acid solutions by soluble sulphates or free sulphuric acid; the precipitation is complete, even with calcium, if alcohol be added to the solution. The hydroxides of the alkaline earths, which are more or less soluble in water, are only precipitated by sodium or potassium hydroxide from concentrated solutions. In solutions of barium salts hydrofluosilicic acid produces a crystalline precipitate of barium silicofluoride, $BaSiFl_6$, and potassium chromate one of barium chromate, $BaCrO_4$.

Kohlrausch and Rose determined, by means of the electric conductivity of solutions, the solubility of many of the salts which have been mentioned—the so-called insoluble salts. They found that a liter of water at 15° dissolved 0.1 mg. of silver iodide; 0.4 mg. of silver bromide; 0.5 mg. of mercuric iodide; 1.7 mg. of silver chloride; 3.1 mg. of mercurous chloride; 2.6 mg. of barium sulphate; 107 mg. of strontium sulphate; 2070 mg. of calcium sulphate; 13 mg. of calcium carbonate; 24 mg. of barium carbonate; 3.8 mg. of barium chromate; 0.2 mg. of lead chromate; 9 mg. of magnesium hydroxide. See Z. f. anorg. Ch. 5 (1894), 237.

The flame colorations produced by the volatile compounds are very characteristic; calcium salts impart a reddish-yellow color; strontium, an intense crimson; barium, a yellowish-green. The spectrum of calcium exhibits several yellow and orange lines, and in addition, a green and a violet line (see the Spectrum Table); that of strontium contains, besides several red lines, an orange and a blue, which are less distinct but very characteristic. Finally, the barium spectrum consists of several orange, yellow, and green lines, of which a bright green is particularly prominent.

DIAMMONIUM COMPOUNDS.

The same relation which ammonia sustains to the univalent alkali metals (p. 296), *hydrazine* or *diamide*, N_2H_4 (pp. 125, 131), discovered by Curtius, bears to the bivalent alkaline earth metals. Diamide, however, does not always act as a di-acid base, which might be inferred from what has been said, for in its most stable derivatives it is as mon-acid as ammonia. It may be assumed that the di-acid compounds contain the bivalent radical *diammonium*, $\overset{II}{N_2H_6}$, the counterpart of the radical ammonium, and that they accordingly arrange themselves with the salts of barium, strontium and calcium. The similarity of diammonium to the alkaline earth metals is shown also in the difficult solubility of the sulphate and by its inability to form alums.

Again, diamide manifests properties allying it with the alkali metals. Its hydrate, $N_2H_4 . H_2O = N_2H_5OH$, generally behaves like a mon-acid base. Its chloride, $N_2H_6Cl_2$, breaks down below 100° into hydrochloric acid and the chloride N_2H_5Cl, which does not yield any more hydrochloric acid unless destroyed by heating. The hydrate $N_2H_4 . 2H_2O = N_2H_6(OH)_2$ is only stable in aqueous solution and upon evaporation changes to $N_2H_4 . H_2O = N_2H_5OH$, boiling without decomposition. It forms but one nitrate of the composition $N_2H_4 . HNO_3$, but one sulphocyanide $N_2H_4 . HCNS$, and but one diammonium nitride, $N_2H_4 . N_3H$.

It would therefore appear that both the bivalent radical N_2H_6 and the univalent radical N_2H_5 are present in the compounds of diamide, and further that those containing the radical N_2H_5 are the more stable derivatives.

Unstable Diammonium Compounds.

$N_2H_6\left\{\begin{matrix}OH\\OH\end{matrix}\right.$	$N_2H_6\left\{\begin{matrix}Cl\\Cl\end{matrix}\right.$	$N_2H_6\left\{\begin{matrix}I\\I\end{matrix}\right.$	$N_2H_6SO_4$.
Dihydrate.	Dichloride.	Di-iodide.	Sulphate.

Stable Diammonium Compounds.

N_2H_5OH	N_2H_5Cl	N_2H_5I	$(N_2H_5)_2SO_4$
Mono-hydrate.	Mono-chloride.	Mono-iodide.	Semi-sulphate.
	$N_2H_5NO_3$.		
	Nitrate.		

The hydrazine salts generally crystallize well. Their great reducing power is one of their characteristics. They precipitate metallic silver from ammoniacal silver solutions; cuprous oxide and metallic copper from alkaline copper solutions (Fehling's solution), and gold from acid solutions of gold chloride (distinction from hydroxylamine). The hydrazine salts are very poisonous. With care nitrous acid will liberate hydrazoic acid from them:

$$N_2H_4 + HNO_2 = N_3H + 2H_2O,$$

otherwise nitrogen. The addition of copper sulphate to the solutions of hydrazine salts causes the separation of a sparingly soluble double salt $CuSO_4 . (N_2H_5)_2SO_4$; this can be used to separate hydrazine from its solutions and from mixtures. The corresponding double salts, with the salts of nickel, cobalt, iron, manganese, cadmium and zinc, are also soluble with difficulty and are anhydrous. For the detection by means of benzaldehyde (benzalazine, m. p. 93°) see Organic Chemistry. Consult Curtius and Schrader, Jr. prakt. Ch. 50 (1894), 311.

Diammonium Sulphate, $N_2H_4 . H_2SO_4 = \overset{II}{(N_2H_6)}SO_4$, can be made by treating solutions of all the other hydrazine salts with sulphuric acid. It consist of vitreous plates, which are soluble in about 33 parts of water at 20°. They deflagrate when quickly heated.

Diammonium Chloride, $N_2H_4 . 2HCl = \overset{II}{(N_2H_6)}Cl_2$, obtained by transposing the sulphate with barium chloride, forms large, vitreous octahedra. It is very soluble in water. It melts with decomposition at about 200°. At 100° it passes gradually into monohydrate.

Hydrazine Hydrate, (diammonium monohydrate), $N_2H_4 . H_2O = \overset{I}{(N_2H_5)}OH$, can be obtained by distilling hydrazine sulphate with caustic potash. It is a strongly refracting, not very mobile liquid, which fumes in the air and boils at 118.5° under 739.5 mm. pressure. It has a faint odor, not reminding one of ammonia, has a caustic taste, is hygroscopic and attracts carbon dioxide from the air. Below —40° it solidifies to a leafy crystalline mass. Its specific gravity equals 1.03 at 21°. It sinks in water and only mixes with it after some time. It can be preserved in a pure condition and in concentrated solution. Dilute aqueous solutions decompose completely in the course of time. Its solution and its vapors color red litmus blue. It breaks down (from its vapor density) at 171° and 760 mm. pressure into hydrazine and water, but on the other hand it vaporizes in a vacuum at 100° without decomposition. It has a powerful reducing action upon many oxides; with chromic acid and mercuric oxide it causes explosion. Nothing definite is known as to its chemical constitution. [See Curtius and Schulz, Jr. prakt. Ch. **42** (1890), 521; Curtius and Schrader, *ibid.* **50** (1894), 318]. Upon distilling the hydrate with barium oxide under reduced pressure the diamide boiling only at 5½° lower, is set free. It fumes strongly in the air and is combustible.

Diammonium Monochloride, $N_2H_4 . HCl = \overset{I}{(N_2H_5)}Cl$, results when the dichloride is heated. It crystallizes in long white needles, melting at 89°. It is very soluble in water.

Diammonium Semisulphate, $(N_2H_4)_2 . H_2SO_4 = \overset{I}{(N_2H_5)}_2SO_4$, is formed upon neutralizing hydrazine hydrate with sulphuric acid. It crystallizes in large, deliquescent plates, melting at 85°.

Another remarkable body is the **Diammonium Nitride**, $N_5H_5 = N_2H_4 . N_3H = \overset{I}{(N_2H_5)}N_3$, prepared by Curtius from ammonium nitride and hydrazine hydrate. It is the ammonium salt of hydrazoic acid. The other salt, $N_8H_6 = N_2H_4 . (N_3H)_2 = \overset{II}{(N_2H_6)}(N_3)_2$, corresponding to the dichloride described above, could not be obtained. Diammonium nitride (diammonium monazide, if the salts of hydrazoic acid are designated *azides*) consists of large, vitreous prisms, melting at about 50°, deliquescing in the air and volatilizing at the ordinary temperature, but more readily with aqueous and alcoholic vapors. The salt dissolves with difficulty in alcohol. When ignited it burns quietly with a yellow flame, without smoke and without residue. If heated rapidly in the air, by contact with a wire raised to a white heat by ignition with detonating metallic azides or fulminating mercury, a powerful explosion will take place even if the salt has deliquesced [Ber. **24** (1891), 3348; see also Ammonium Nitride, p. 298.]

2. METALS OF THE MAGNESIUM GROUP.

In this group are usually included beryllium, magnesium, zinc, and cadmium. However, these metals do not exhibit complete analogy, as is clearly seen from their position in the periodic system (p. 300). Beryllium shows the greatest variations. It approaches aluminium, while magnesium resembles not only zinc and cadmium, but also the alkaline earth metals, calcium, strontium, and barium. Its similarity to the latter is expressed by the basic nature of its oxide, whereas it resembles zinc and cadmium mainly in isomorphism of compounds.

Beryllium and magnesium bear the same relations to calcium, strontium, and barium, as lithium and sodium bear to the metals of the potassium group.

The alkaline character of the alkaline earth metals gradually diminishes from barium to calcium, and becomes almost nothing in magnesium and beryllium, which possess the lowest atomic weights (see p. 300). Magnesium and beryllium are scarcely capable of decomposing water, even at boiling temperatures. Their oxides and hydroxides are almost insoluble in it; the hydroxides decompose, on gentle ignition, into oxides and water. Their carbonates are very unstable; their chlorides, too, suffer a partial decomposition into oxide and hydrogen chloride, even on drying. The solubility of the sulphates of magnesium and beryllium further distinguishes them from the metals of the alkaline earth group.

The specific properties of beryllium and magnesium are maintained in zinc and cadmium, which constitute a natural group with the former. Zinc and cadmium do not decompose water at a boiling heat; their hydroxides are insoluble in it, and are not very stable; their carbonates and chlorides easily undergo decomposition; their sulphates are readily soluble in water. The similarity is further expressed by the isomorphism of most of their compounds. Thus, magnesium and zinc sulphates crystallize with seven molecules of water, in perfectly similar forms. If the solution of a mixture of both salts be allowed to crystallize, we get crystals with variable quantities of zinc and magnesium: the formation of such *isomorphous mixtures* in *ad libitum* proportions is a characteristic indication of the isomorphism of compounds chemically similar (p. 255).

The difference between beryllium and magnesium upon the one side, and zinc and cadmium on the other, is shown distinctly in their specific gravities. While the first two elements possess a low specific gravity (Be 1.8, Mg 1.74), zinc and cadmium (with specific gravities of 7.1 and 8.6) belong to the so-called *heavy metals* (see p. 252).

The difference in specific gravity determines, also, many differences in chemical character. The light metals (especially the alkalies and alkaline earths) form rather unstable sulphides, readily soluble in water, while the sulphides of zinc and cadmium, like those of all heavy metals, are insoluble in water, and usually in dilute acids; hence magnesium and beryllium are not, while zinc and cadmium are, precipitated by hydrogen sulphide or alkaline sulphides as sulphides from solutions of their salts. Further, the oxides of the light metals are very stable, and are only reduced by ignition with carbon if they are readily fusible (like potassium and sodium oxides); the heavy metals, on the other hand, are easily separated from their oxides by carbon. Zinc and cadmium oxides are reduced by carbon, while those of magnesium and beryllium are not altered.

1. MAGNESIUM.

$Mg = 24.36.$

Magnesium is very abundant in nature, and almost always accompanies calcium in its compounds. As carbonate, it occurs in compact masses, as magnesite, etc. Dolomite, which forms entire mountains, is an isomorphous mixture of calcium and magnesium carbonates. Magnesium is also present in most of the natural silicates; its soluble salts are contained in almost all natural waters. In conjunction with the alkali salts they constitute the most important salts of the Stassfurt beds (see p. 276).

Metallic magnesium may be obtained by the electrolysis of the chloride (Bunsen, 1852) or by heating the same with sodium (Bussy, 1830). It is more easily prepared by heating the double chloride of magnesium and sodium with metallic sodium and fluorspar, the latter serving merely as a flux:

$$MgCl_2 . NaCl + 2Na = 3NaCl + Mg.$$

At present magnesium is obtained in large quantities by the electrolysis of fused carnallite [see Dammer, Chemische Technologie, Bd. II, (1895)].

Magnesium is a brilliant, almost silver-white metal, of specific gravity 1.74. It is tenacious and ductile, and when heated may be converted into wire and rolled out into thin ribbons. It melts at about 700°, and distils at a bright-red heat. At ordinary temperatures, it scarcely oxidizes in the air; it burns, when heated, with an extremely intense white light, owing to the glowing non-volatile magnesium oxide. Magnesium light is rich in chemically active rays, and, for this reason, it is employed in photography for artificial illumination. Its alloy with zinc is generally employed as a substitute for pure magnesium, as it burns with an equally bright light. Its intense light has led to its use in pyrotechny. Boiling water is very slowly decomposed by magnesium. It dissolves easily in dilute acids, forming salts; the alkalies do not attack it. Many metallic oxides and acids when heated with magnesium powder lose their oxygen and are reduced by it (see p. 237).

Magnesium Oxide, MgO, or *magnesia*, formed by the combustion of magnesium, is ordinarily obtained by the ignition of the hydroxide or the carbonate (*Magnesia usta*). It is a white, very voluminous, amorphous powder, which finds application in medicine. The feebly ignited magnesia combines with water, with slight generation of heat, to produce magnesium hydroxide.

In Stassfurt the magnesium chloride liquors, produced in the preparation of potassium chloride, are utilized in producing a very good magnesia, which is used in the manufacture of fire-brick or fire-clay (p. 276).

At high temperatures magnesia conducts electricity and it can be made to glow and become luminous by the current. If, therefore, little thin cylinders of magnesia are heated until they reach the point of conductivity they will answer for the production of the electric light (Nernst).

Magnesium Hydroxide, $Mg(OH)_2$, is precipitated from solutions of magnesium salts by potassium or sodium hydroxide as a gelatinous mass. Dried at 100° it is a white amorphous powder. It is almost insoluble in water and alkalies; moist red litmus-paper is, however, colored blue. Ammonium salts dissolve it quite easily, forming soluble double salts. Magnesium hydroxide attracts carbon dioxide from the air and forms magnesium carbonate. It yields the oxide and water when gently ignited.

Magnesium Chloride, $MgCl_2$, is present in traces in many mineral springs. It may be prepared by the solution of the carbonate or oxide in hydrochloric acid; in large quantities it is obtained as a by-product in the technical production of potassium chloride. When its solution is evaporated the salt crystallizes out with six molecules of water in deliquescent crystals, isomorphous with calcium chloride. When these are heated they give up water, and there occurs at the same time a partial decomposition of the chloride into oxide and hydrogen chloride:

$$MgCl_2 + H_2O = MgO + 2HCl.$$

As magnesium chloride is produced in large quantities in various technical processes, repeated efforts have been made to utilize the above reaction for the preparation of hydrochloric acid, by conducting steam over heated magnesium chloride.

Lately the liquors have been evaporated and the magnesium chloride dehydrated, whereby it breaks down in part into hydrochloric acid and magnesium oxide. When the residual magnesium oxychloride is heated in an air current, magnesia and chlorine are produced (Weldon-Pechiney; see p. 50).

To get anhydrous magnesium chloride, ammonium chloride is added to the solution of the former. The double salt, $MgCl_2 . NH_4Cl + 6H_2O$, is formed. When this is heated it first loses water, and at 460° throws off ammonium chloride, leaving anhydrous magnesium chloride. The latter can also be obtained by heating the hydrated salt in a current of hydrochloric acid. This is a leafy, crystalline mass, which fuses at 708°, and distils undecomposed at a red heat; it is very deliquescent in the air.

Double salts, similar to the above, are also formed from potassium and calcium chloride. The potassium double salt, $MgCl_2 . KCl + 6H_2O$, occurs in considerable deposits as carnallite at Stassfurt (p. 276).

Magnesium Sulphate, $MgSO_4$, is found in sea-water and in many mineral springs. With more or less water it is *kieserite*, which abounds extensively at Stassfurt. At ordinary temperatures it crystallizes with seven molecules of water, $MgSO_4 + 7H_2O$, in four-sided rhombic prisms, readily soluble in water (at 0° in 2 parts of water). It has a bitter, salt-like taste, and serves as an aperient. It crystallizes with six molecules of water from solutions heated to 70°; at 0°, however, it has twelve molecules. When heated to 150° these hydrates lose all their water of crystallization, excepting *one molecule*, which escapes above 200°. *One* molecule of water, in magnesium sulphate, is, therefore, more closely combined than the rest. Many other salts containing water deport themselves similarly. The more intimately combined water is termed *water of constitution.*

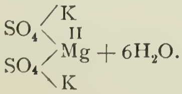
Magnesium sulphate forms double salts with potassium and ammonium sulphates, which crystallize with six molecules of water in monoclinic prisms, *e. g*:

$$MgSO_4 . K_2SO_4 + 6H_2O.$$

The sulphates of zinc and several other metals, *e. g.*, iron, cobalt, and nickel, in their bivalent forms, are very similar to magnesium sulphate. Their sulphates crystallize with seven molecules of water, and are isomorphous. They form double salts with potassium and ammonium sulphates; these crystallize with six molecules of water, and are isomorphous, *e. g.*:

$$ZnSO_4 + 7H_2O \qquad ZnSO_4 . K_2SO_4 + 6H_2O.$$
$$FeSO_4 + 7H_2O \qquad FeSO_4 . K_2SO_4 + 6H_2O.$$

The constitution of these double salts may be viewed in the same way as that of potassium-sodium sulphate, or of mixed salts of polybasic acids. We may suppose that in the given instance the bivalent metal unites two molecules of sulphuric acid:



$$\begin{array}{l} \mathrm{SO_4}\begin{array}{l}\diagup\mathrm{K}\\ \diagdown\end{array} \\ \qquad\overset{\mathrm{II}}{\mathrm{Mg}} + 6\mathrm{H_2O}. \\ \mathrm{SO_4}\begin{array}{l}\diagup\\ \diagdown\mathrm{K}\end{array}\end{array}$$

Magnesium Phosphates.—The *tertiary* phosphate $Mg_3(PO_4)_2$, accompanies the tertiary calcium phosphate in small quantities in bones and in plant ashes. The *secondary* phosphate, $MgHPO_4 + 7H_2O$, is precipitated from the soluble magnesium salts, by disodium phosphate (Na_2HPO_4) as a salt dissolving with difficulty in water. In the presence of ammonia and ammonium salts, *magnesium-ammonium phosphate*, $MgNH_4PO_4 + 6H_2O$, is precipitated as a crystalline powder insoluble in water. This double salt is found in guano, forms in the decay of urine, and is sometimes the cause of the formation of calculi. The *primary* salt, $MgH_4(PO_4)_2$, has not been obtained.

The magnesium salts of arsenic acid, H_3AsO_4, are very similar to those of phosphoric acid. Magnesium-ammonium arseniate, $MgNH_4AsO_4 + 6H_2O$, is likewise almost insoluble in water.

Magnesium Carbonate, $MgCO_3$, occurs in nature as magnesite, crystallized in rhombohedra (isomorphous with calcite), or more often in compact masses. Combined with calcium carbonate, it forms dolomite, to which, when pure, is ascribed the formula, $CaCO_3.MgCO_3$; however, it usually contains an excess of calcium carbonate. On adding sodium or potassium carbonate to the aqueous solution of a magnesium salt, some carbon dioxide escapes, and a white precipitate forms, which consists of a mixture of magnesium carbonate and hydroxide. If the precipitate be dried at low temperature, we obtain a white, voluminous powder, whose composition generally corresponds to the formula $Mg(OH)_2.3MgCO_3 + 4H_2O$. This salt is employed under the name *Magnesia alba* in medicine. If it be suspended in water, and carbon dioxide passed through it, the salt will dissolve, and upon standing exposed to the air, crystals of *neutral carbonate*, $MgCO_3 + 3H_2O$, separate. When these are boiled with water they give up carbon dioxide and are again converted into the basic carbonate. The naturally occurring magnesite sustains no change when boiled with water, and it is only when it is heated above 300° that it decomposes into magnesium oxide and carbon dioxide.

Freshly prepared magnesium carbonate dissolves in acid alkaline carbonates and crystallizes from them as $4MgCO_3 + 15H_2O$.

Magnesium carbonate yields isomorphous double salts, with potassium carbonate and ammonium carbonate; *e. g.*, $MgCO_3.K_2CO_3 + 4H_2O$.

Of the *silicates* of magnesium, we may mention olivine (Mg_2SiO_4), serpentine ($Mg_3Si_2O_7 + 2H_2O$), talc ($Mg_3Si_4O_{11} + H_2O$), sepiolite or meerschaum ($Mg_2Si_3O_8 + 2H_2O$). The mixed silicates of magnesium and calcium are very numerous; to these belong asbestos, the augites and horn-blendes.

Magnesium Nitride, Mg_3N_2 (pp. 116, 124, 126), is a light, porous, yellow-colored mass. Briegleb and Geuther found that it was produced when magnesium was heated in a current of ammonia:

$$Mg_3 + 2NH_3 = Mg_3N_2 + 3H_2.$$

It is also obtained pure when magnesium is heated in nitrogen. When introduced into water, the latter is made to boil and large volumes of ammonia escape [see Paschkowezky, Jr. prakt. Ch. 47 (1893), 89].

Recognition of Magnesium Compounds.—The fixed alkaline hydroxides precipitate magnesium hydroxide from soluble magnesium salts; the carbonates throw down basic magnesium carbonate. The precipitates are insoluble in pure water and the alkalies, but dissolve readily in solutions of ammonium salts. In the presence of the latter, neither the alkaline hydroxides nor carbonates cause precipitation. In the presence of ammonia and ammonium chloride, disodium phosphate precipitates magnesium-ammonium phosphate, $MgNH_4PO_4 + 6H_2O$, insoluble in water.

2. BERYLLIUM.

Be = 9.1.

Among the metals of the second group beryllium occupies a position similar to that of lithium in the first group (pp. 272, 299); in both elements, which have the lowest atomic weight in their group, the specific group character is considerably diminished, or does not find expression. As lithium attaches itself in many respects to magnesium, so does beryllium approach aluminium. Like the latter, it is scarcely at all attacked by nitric acid, but dissolves easily in sodium or potassium hydroxide, with elimination of hydrogen. Like aluminium oxide, that of beryllium dissolves in the alkalies, and is almost invariably accompanied by the former in its natural compounds. However, beryllium, in most of its compounds, stands nearer to magnesium than to aluminium. The determination of the vapor density of beryllium chloride (see below) and of certain organic derivatives has finally established the atomic weight and the valence of this element.

Beryllium is not very abundant in nature and is found principally in beryl, a double silicate of aluminium and beryllium, $Al_2Be_3(SiO_3)_6$. Emerald has the same composition, and is only colored green by a slight amount of chromium oxide.

It was in these minerals that Vauquelin discovered beryllium in 1797. It is also present in leucophane (a silicate), together with aluminium, fluorine and sodium; and in gadolinite (a silicate) with ferrous oxide, yttrium, cerium, lanthanum, and other rare earths.

Metallic beryllium is obtained by the ignition of the chloride, or better, potassium beryllium chloride (or potassium beryllium fluoride, $BeFl_2 . 2KFl$), with sodium, and by the electrolysis of $BeFl_2 . KFl$. It is a white, ductile metal, of specific gravity 1.8. Its specific heat at the ordinary temperature equals 0.408; the atomic heat is, therefore, 3.7 (p. 254). It does not decompose water, even upon boiling. It does not oxidize in the air at ordinary temperatures. When finely divided and heated it will burn in the air with a very bright light. It is readily dissolved by dilute hydrochloric and sulphuric acids; also by potassium and sodium hydroxides.

Beryllium Chloride, $BeCl_2$, is obtained, like aluminium chloride, by the ignition of a mixture of beryllium oxide and carbon in a stream of chlorine. It sublimes in shining needles, which deliquesce in the air. Its vapor density corresponds to the molecular formula $BeCl_2 = 79.9$ (Nilson). Pure beryllium chloride dissolves in water, forming a colorless solution, from which it crystallizes with four molecules of water; upon drying it suffers a decomposition similar to that of magnesium chloride.

The salts of beryllium have a sweet taste, hence it has been called *glucinum*. Ammonium hydroxide precipitates a white, gelatinous *beryllium hydroxide*, $Be(OH)_2$, from solutions of the soluble salts. This dissolves readily in sodium and potassium hydroxide, and in a mixture of ammonia and ammonium carbonate, but on boiling, separates again from solution. When heated, the hydroxide breaks down into water and *beryllium oxide*, BeO, which is a white, amorphous powder, of specific gravity 2.96.

Beryllium Sulphate, $BeSO_4$, crystallizes from water at various temperatures, with four or seven molecules of water; it contains two molecules at 105°, and is anhydrous at

250–260°. It does not crystallize with magnesium sulphate in an isomorphous mixture. The double salt, $BeSO_4 . K_2SO_4 + 2H_2O$, does not dissolve readily in water. Compare Krüss and Moraht, Ber. **23** (1890), 727, and Ann. Chem. **262** (1891), 38.

3. ZINC.

$Zn = 65.4$.

The natural compounds of the heavy metals have generally a high specific gravity, frequently possess metallic luster, usually occur in the older crystalline rocks in veins, and are termed *ores*. The most important zinc ores are the carbonate, $ZnCO_3$, the silicate, and sphalerite or blende, ZnS. The principal sources of these ores are in Silesia, England, Belgium, Poland, the United States, France, and Spain. To get the metal the carbonate or sulphide is converted into oxide by roasting it in the air; the product is then mixed with carbon and ignited in cylindrical clay tubes. In this manner the oxide is reduced:

$$ZnO + C = Zn + CO,$$

and the liberated zinc distilled off. The receivers contain the fused, compact zinc and a gray, pulverulent mass, called *zinc-dust*, which consists of a mixture of zinc oxide with finely divided metal. This material is used in laboratories as a strong reducing agent. See Mylius and Fromm on the purification of zinc, Z. f. anorg. Ch. **9** (1895), 144.

Metallic zinc has a bluish-white color, and exhibits rough, crystalline fracture; its specific gravity equals 7–7.1. At ordinary temperatures it is brittle and can be pulverized; at 100–150° it is malleable and can be rolled into thin leaves and drawn out into wire. At 200° it becomes brittle again and may be easily broken. It melts at 420° and distils at about 950°.

It becomes coated with a thin layer of basic carbonate in moist air. Heated in the air it burns to zinc oxide with a very intense, bluish-white light. Compact zinc will only decompose water at a red heat; zinc-dust, however, acts at ordinary temperatures. Perfectly pure zinc is only slowly attacked by dilute acids at the ordinary temperature; it dissolves by boiling with potassium or sodium hydroxide, as well as ammonia, with liberation of hydrogen:

$$Zn + 2NaOH = Zn(ONa)_2 + H_2.$$

Owing to its slight alteration in the air zinc meets with extensive application as sheet-zinc for coating statues and in architectural adornment, and in galvanizing sheet-iron. It also forms an important constituent of many valuable alloys, such as brass and argentan (see these).

Zinc Hydroxide, $Zn(OH)_2$, is precipitated as a white, amorphous powder, from aqueous solutions of zinc salts, by alkalies, and is soluble in excess of the reagent. When heated it decomposes into water and zinc oxide.

Zinc Oxide, ZnO, is usually prepared by igniting the precipitated basic carbonate, and, as *zinc white*, is employed as a stable white paint. The oxide obtained by burning the metal is a white, voluminous, flocculent mass, called *Flores zinci*, or *Lana philosophica*. When zinc oxide is heated it acquires a yellow color, which disappears on cooling.

Zinc oxide occurs in nature as *zincite*, colored by impurities.

Zinc Chloride, $ZnCl_2$ (*Zincum chloratum*), anhydrous, is obtained by heating zinc in a stream of chlorine, by the evaporation of the solution of zinc in hydrochloric acid, and by the distillation of zinc sulphate with calcium chloride. It forms a white, deliquescent mass, which fuses when heated and distils at about 730°. Molten zinc chloride is a transparent, very mobile, strongly refracting liquid, attracting moisture more readily than phosphoric anhydride [Lorenz, Z. f. anorg. Ch. **10** (1895), 82]. It crystallizes from concentrated hydrochloric acid solution with one molecule of water in deliquescent octahedra. When the aqueous solution of zinc chloride is evaporated it partly decomposes (like magnesium chloride) into zinc oxide and hydrochloric acid. When the concentrated zinc chloride is mixed with zinc oxide, a plastic mass is obtained, which hardens rapidly; a mixture of magnesium chloride and oxide does the same. In both instances the hardening depends upon the formation of basic oxychlorides, *e. g.*, $Zn<^{Cl}_{OH}$. Zinc chloride forms deliquescent double salts with the alkaline chlorides, *e. g.*, $ZnCl_2.2KCl$. With ammonia it yields various compounds, of which $ZnCl_2.NH_3$ is characterized by great stability.

Zinc Sulphate, $ZnSO_4$, is obtained by dissolving zinc in sulphuric acid. It is prepared upon a large scale by carefully roasting zinc-blende (ZnS); the zinc sulphate is extracted by water. It crystallizes at ordinary temperatures from aqueous solutions with seven molecules of water (zinc or white vitriol, *Zincum sulphuricum*) in rhombic crystals, resembling those of magnesium sulphate. It affords double salts with the alkaline sulphates; these contain six molecules of water (p. 315).

Zinc Carbonate, $ZnCO_3$, occurs native as smithsonite in hexagonal crystals, isomorphous with those of calcite. Sodium carbonate precipitates a mixture of $ZnCO_3.H_2O$, which rapidly becomes crystalline, and the basic carbonate $2ZnCO_3.3Zn(OH)_2.H_2O$.

Zinc Sulphide, ZnS, is zinc-blende or sphalerite, usually colored brown by ferric oxide or other admixtures. Ammonium sulphide precipitates it as a white compound from zinc solutions. Although fused zinc reacts with difficulty with sulphur, zinc-dust combines with the latter in powdered form quite readily, and if the mixture be heated or struck with a hammer the union is accompanied by an explosion. Zinc sulphide is insoluble in water, but is readily dissolved by dilute acids, excepting acetic acid; therefore it may be precipitated by hydrogen sulphide from zinc acetate solutions. This reaction serves to separate zinc from other metals. The sulphide is also applied as a white pigment; especially a mixture of it with barium sulphate (lithopone—made from zinc sulphate and barium sulphide).

Zinc Silicate, $Zn_2SiO_4 + H_2O$, occurs in rhombic crystals as calamine. In the analytical way zinc is characterized by the fact that its hydroxide dissolves both in caustic soda and potash as well as in ammonia; hydrogen sulphide precipitates white zinc sulphide from these solutions.

4. CADMIUM.

$Cd = 112$.

Cadmium very often accompanies zinc in its ores. As much as 5 per cent. of this metal is present in the Silesian zinc ores; it was first discovered in them in 1817 by Hermann; shortly after Stromeyer recognized it as a new element. Being more volatile than zinc, in obtaining the latter it distils off first, and may be easily separated from the first portions of the distillate. It is a white, tenacious, and rather soft metal, of specific gravity 8.6. It fuses at 320° and boils at 770°. It does not alter much in the air. Heated, it burns with the separation of a brown smoke of cadmium oxide. It dissolves with difficulty in dilute hydrochloric and sulphuric acids, but readily in nitric acid. Zinc throws out the metal from solutions of the soluble cadmium salts.

St. Claire Deville found the specific gravity of cadmium vapors at 1040° and H. Biltz at about 1700° to approximate closely 112 ($O_2 = 32$). Therefore, the molecular weight of cadmium is 112. Since the atomic weight of cadmium (determined from its specific heat) is also 112, it follows that the gas molecule of cadmium consists of but *one* atom. We know that the molecules of other elements in the gaseous state are composed of two or more atoms (O_2, N_2, P_4). Cadmium, therefore, forms an exception to this rule. This is also true of mercury, zinc and perhaps, too, of other bivalent metals. These relations remind us of the behavior of the hydrocarbon residues (radicals); while the bivalent or quadrivalent groups, *e. g.*, ethylene, C_2H_4, and acetylene, C_2H_2, exist in free condition, the univalent groups (as CH_3 and CN) cannot appear free, but double themselves when separated from their compounds.

Cadmium Hydroxide, $Cd(OH)_2$, is precipitated as a white powder, from the soluble cadmium salts, by the alkalies; it is insoluble in sodium and potassium hydroxides, but dissolves readily in ammonium hydroxide.

Cadmium Oxide, CdO, is prepared by igniting the nitrate. It is a brownish-black powder, consisting of microscopic octahedra. When obtained by heating the carbonate or hydroxide, it is a brown, amorphous powder.

Cadmous Hydroxide CdOH, and its *oxide*, Cd_2O, have been prepared. The first is a grayish-white compound, while the second is composed of yellow, translucent crystals. It is obtained on heating the hydroxide to a temperature at which sulphuric acid gives off dense white fumes. The hydroxide is a reducing agent, yielding hydrogen with hydrochloric acid and oxides of nitrogen with nitric acid. The oxide conducts itself similarly. These compounds are of interest, as they foreshadow the tendency toward the formation of lower oxides, so strongly shown by mercury (*Am. Chem. Jr.*, 12, 493 .

Cadmium Chloride, $CdCl_2$, crystallizes from aqueous solution, with two molecules of water, and may be dried without decomposition. The anhydrous salt melts at 540° and sublimes in scales.

Cadmium Iodide, CdI_2, is obtained by the direct action of iodine upon metallic cadmium in the presence of water. It crystallizes from the latter in hexagonal tables. It is used in photography.

Cadmium Sulphate, $CdSO_4$, crystallizes at —20°, like the sulphates of zinc and magnesium at the ordinary temperature, with seven molecules of water, but at the ordinary temperature with $\frac{8}{3}$ molecules of water; the crystals effloresce in the air. It, however, forms double salts with the sulphates of the alkali metals, *e. g.*, $CdSO_4 . K_2SO_4 + 6H_2O$; these are perfectly analogous to those of zinc and magnesium, and isomorphous with them (p. 319).

Cadmium Sulphide, CdS, occurs native as greenockite, in yellow hexagonal prisms. Hydrogen sulphide precipitates it from cadmium salt solutions as a yellow powder, insoluble in dilute acids. It is employed as a pigment.

Almost all the alloys of cadmium have a low melting point. Freshly prepared cadmium amalgam is a white plastic mass, which soon becomes hard; it was formerly used for filling teeth.

The magnitude of the atomic weight of **Mercury** would place the latter in the group of zinc and cadmium. The relationship of these three heavy metals occupying a similar position in the three great periods are, from a physical point of view, distinguished among the heterologous members by their ready fusibility and volatility, which nearly reach a maximum in them. In the homologous series, zinc, cadmium, mercury, these properties increase with rising atomic weight (just as with the metals of the potassium group, p. 272):

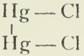
	Zn	Cd	Hg
Atomic weight,	65.4	112	200.3
Melting point,	420°	320°	—39.5°
Boiling point,	950°	770°	357°
Specific gravity,	7.1	8.6	13.5
Atomic volume,	9.1	13	14.7

The gradation in the heat of formation of their compounds (p. 327) clearly indicates that mercury must be arranged in a group with cadmium and zinc.

Like zinc and cadmium, it yields compounds of the form HgX_2, in which it appears bivalent. These derivatives are, in many respects, similar to the corresponding compounds of zinc and cadmium. Thus, mercuric sulphate forms double salts with the alkaline sulphates, which crystallize with six molecules of water ($HgSO_4 . K_2SO_4 + 6H_2O$), and are isomorphous with the double sulphates of the magnesium group (p. 315). The similarity, however, limits itself to few compounds. Since the properties of each group sustain a slight change by virtue of the increasing atomic weight, we are not surprised to observe this to be very evident in the case of mercury (with the high atomic weight 200.3), especially as the middle (transition) member of the third great period is not known (p. 245). Mercury differs essentially from zinc and cadmium in that, in addition to the compounds of the form $\overset{II}{Hg}X_2$ (mercuric compounds), it is also capable of yielding those of the form $\overset{I}{Hg}X$ (mercurous compounds), in which it seems to be univalent. Here we meet an instance, frequently observed, in which one and the same metal (as with the most metalloids) is capable of forming compounds of two or more forms, which are to be referred to a different valence of the metal; and it often happens that the derivatives of a metal, appearing in different forms or types, are frequently more essentially distinguished from one another than the compounds of different elements having the same type. Thus, the mercuric compounds ($\overset{II}{Hg}X_2$) are similar to those of zinc and cadmium, after the same form, while the mercurous compounds ($\overset{I}{Hg}X$) exhibit great resemblance to the cuprous ($\overset{I}{Cu}X$) and silver ($\overset{I}{Ag}X$) compounds, constituted according to a similar type.

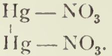
It shows that the similarity of the compounds is influenced not only by the nature of the metals, but frequently, to a marked degree, by the forms or types according to which they are constituted (p. 330).

Heretofore it has been generally customary to assume the presence of two atoms of mercury, united to a bivalent group, in the molecule of the mercurous derivatives; hence the appearance of a univalent character:



$$\begin{array}{l} Hg - Cl \\ | \\ Hg - Cl \end{array}$$

Chloride.



$$\begin{array}{l} Hg - NO_3 \\ | \\ Hg - NO_3. \end{array}$$

Nitrate.

The most recent researches, however, show that these compounds can be represented by the simple formulas $HgCl$, $HgNO_3$; see pp. 325, 332.

5. MERCURY.

$Hg = 200.3.$

Mercury (*Hydrargyrum, i. e., water-silver*) occurs in nature principally as the sulphide, *cinnabar;* more rarely native in the form of little drops scattered through rocks. Its most important localities are Almaden, in Spain; New Almaden, in California; Idria, in Austria; Tuscany, in Italy; Mexico; Peru; China; Japan. Considerable quantities have been found also in Russia.

The metallurgical separation of mercury is very simple. Cinnabar is roasted in reverberatory furnaces, whereby the sulphur burns to dioxide, and the mercury vapors are condensed in large chambers with the aid of water. There is a regular and gradual return to the old method of distilling cinnabar with lime or iron from iron retorts. Commercial mercury usually contains a slight quantity of other metals dissolved in it. For its purification, it is poured in a thin stream into a deep layer of dilute nitric acid or of ferric chloride solution, or it is shaken with a solution of potassium dichromate and dilute sulphuric acid, by which the admixed metals are more easily dissolved than the mercury. Finally, the metal is passed through chamois skin and distilled (best in a vacuum). Ber. **12** (1879), 204, 576.

Mercury is the only metal which is liquid at ordinary temperatures. At 0° its specific gravity equals 13.596 and at 15°, 13.559; it solidifies at —39.5°, and crystallizes in regular octahedra; it evaporates somewhat at medium temperatures, and boils at 357°. Its vapors are very poisonous. The specific gravity of the vapor of mercury is 200.3, ($O_2 = 32$). Therefore, the molecular weight of the metal is 200.3, and as its atomic weight is also 200.3, the molecule, like that of cadmium and zinc, is composed of only *one* atom. At ordinary temperatures, mercury is not altered by exposure to the air; near the boiling point, however, it gradually oxidizes to red mercuric oxide. Hydrochloric and cold sulphuric acids do not act upon mercury; hot sulphuric acid converts it into mercuric sulphate, with evolution of sulphur dioxide. Even dilute nitric acid will readily dissolve it. It combines with the halogens and sulphur at ordinary temperatures.

Mercury dissolves almost all metals (not iron) forming *amalgams*. It unites with potassium and sodium upon gentle warming, with production of heat and light. When the quantity of potassium and sodium exceeds 2 per cent., the alloy is solid and crystalline; by less amount it remains liquid. [Compare Z. f. phys. Ch. 29 (1899), 119.] Tin amalgam is employed for coating mirrors.

Sodium amalgam may be made by placing rather large pieces of sodium upon the bottom of an iron crucible, covering them with wire gauze, so that they cannot rise to the surface, and pouring mercury upon them. With large quantities the reaction begins cf itself. Finally, heat must be applied while stirring.

Mercury forms two series of compounds, *mercurous* and *mercuric*. The first are analogous to the cuprous, and have the form HgX. In them mercury appears to be univalent. In many respects the mercurous compounds are similar to the cuprous and silver derivatives. The halogen compounds are insoluble, and darken on exposure to light.

In the mercuric derivatives, HgX_2, mercury is bivalent, and is very much like zinc and cadmium. Mercuric compounds almost always form, if the substance reacting with the mercury is in excess; when the opposite is the case, mercurous salts result. Mercuric derivatives, by the addition of mercury, pass into the mercurous, *e. g.*,

$$Hg(NO_3)_2 + Hg = Hg_2(NO_3)_2.$$

This change may also be effected by reducing agents (sulphurous acid, phosphorous acid and stannous chloride). Oxidizing agents convert the mercurous into mercuric compounds.

MERCUROUS COMPOUNDS.

Mercurous Chloride, HgCl or Hg_2Cl_2, calomel (*Hydrargyrum chloratum*), is an amorphous white precipitate, produced by the addition of hydrochloric acid or soluble chlorides to the solution of mercurous salts. It is generally formed by the sublimation of mercuric chloride with mercury; or a mixture of mercuric sulphate, mercury and sodium chloride is sublimed:

$$HgSO_4 + 2NaCl + Hg = Na_2SO_4 + 2HgCl.$$

It then forms a radiating, crystalline mass (quadratic prisms) of specific gravity 7.2. Calomel is insoluble in water, in alcohol, and in dilute acids; it gradually decomposes when exposed to the light, with separation of mercury. When heated, it sublimes without fusing. Boiling hydrochloric acid and hot concentrated solutions of calcium chloride and alkaline chlorides decompose it into mercuric chloride and free mercury:

$$2HgCl = HgCl_2 + Hg.$$

When ammonium hydroxide is poured over calomel, it blackens (hence the name calomel, from *καλομελας*, beautiful black); it is not surely known what chemical change occurs here.

The vapor density of calomel vapors at 400° (first determined by Mitscherlich, and confirmed by Deville and Troost, Rieth and Odling) is 235 ($O_2 = 32$); which corresponds to the formula HgCl. As formerly supposed, and as recently demonstrated by V. Meyer and Harris in opposition to Fileti, calomel breaks down completely into mercury and mercuric chloride [Ber. 28 (1895), 364]. This mixture has the same vapor density that undecomposed calomel would show:

$$\underset{\text{1 vol.}}{HgCl} + \underset{\text{1 vol.}}{HgCl} = \underset{\text{1 vol.}}{Hg} + \underset{\text{1 vol.}}{HgCl_2}.$$

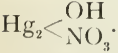
The question, whether the mercurous compounds contain one or two atoms of mercury, whether, for example, the formula Hg_2Cl_2 or HgCl properly belongs to calomel, can, therefore, not be decided by the determination of its vapor density alone. It must also be ascertained of what the vapor consists—and this proof free from objection has not yet been given. From electro-chemical experiments and from the analogy to cuprous and silver chlorides it would seem very probable that mercurous chloride has the simple formula HgCl [Z. f. anorg. Ch. 9 (1895), 442].

Mercurous Nitride, N_3Hg or $Hg_2(N_3)_2$, is formed by adding mercurous nitrate to solutions of hydrazoic acid or its alkali salts. It is insoluble in water. It consists of microcrystalline needles, becoming yellow in the light and blackened by ammonia, just like calomel. When heated or struck it explodes with great violence. Its separation into its elements is accompanied with a brilliant blue light (p. 312).

Mercurous Iodide, HgI or Hg_2I_2, is prepared by rubbing together 8 parts of mercury with 5 parts of iodine, or by precipitating mercurous nitrate with potassium iodide. It is a yellowish-green powder, insoluble in water and in alcohol. Light changes it to mercuric iodide and mercury. Aqueous solutions of potassium iodide have the same effect.

Mercurous Oxide, Hg_2O, is a black mass, and is formed by the action of potassium or sodium hydroxide upon mercurous salts. In the light or at 100° it decomposes into mercuric oxide and mercury.

Mercurous Nitrate, $HgNO_3$ or $Hg_2(NO_3)_2$, is produced by allowing dilute nitric acid to act upon excess of mercury in the cold. It crystallizes with one molecule of water in large monoclinic tables. It dissolves readily in water acidulated with nitric acid; pure water partly decomposes it with the separation of a yellow *basic* salt of the composition



$$Hg_2{<}\begin{matrix}OH\\NO_3\end{matrix}.$$

The nitric acid solution of mercurous nitrate oxidizes when exposed to the air, and gradually becomes mercuric nitrate; this may be prevented by adding metallic mercury to the solution, whereby the resultant mercuric salt is again changed to the mercurous state:

$$Hg(NO_3)_2 + Hg = Hg_2(NO_3)_2.$$

Mercurous Sulphate, $Hg_2(SO_4)$, results when an excess of mercury is heated gently with concentrated sulphuric acid; it separates as a crystalline precipitate, difficultly soluble in water, if sulphuric acid be added to a mercurous nitrate solution. It fuses upon application of heat, and decomposes into sulphur dioxide, oxygen and mercury.

Mercurous Sulphide, Hg_2S, is not definitely known. A black compound is produced in dilute solutions of mercurous nitrate by hydrogen sulphide or alkaline sulphides. It contains mercury and mercuric sulphide:

$$Hg_2S = Hg + HgS.$$

MERCURIC COMPOUNDS.

Mercuric Chloride, $HgCl_2$, corrosive sublimate (*Hydrargyrum bichloratum*), is produced when mercuric oxide is dissolved in hydrochloric acid, or metallic mercury in aqua regia. It is obtained on a large scale by the sublimation of a mixture of mercuric sulphate with sodium chloride:

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

It crystallizes from water in rhombic prisms, and dissolves at medium temperatures in 15 parts of water, at 100° in 2 parts; it is still more soluble in alcohol. Its specific gravity is 5.4. It fuses at 265° and boils at 307°. Its critical pressure is about 420 mm. (p. 229). The vapor density corresponds to the molecular formula $HgCl_2$ (= 271.2).

Reducing substances, like sulphur dioxide and stannous chloride, change it to insoluble mercurous chloride:

$$2HgCl_2 + SO_2 + 2H_2O = Hg_2Cl_2 + H_2SO_4 + 2HCl.$$

Stannous chloride first precipitates mercurous chloride:

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4,$$

which is afterward reduced, by the excess of stannous chloride, to metallic mercury:

$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4.$$

Mercuric chloride is greatly inclined to form double salts with metallic chlorides, *e. g.*, $HgCl_2.KCl + H_2O$. These may be regarded as the salts of a hydrochlormercuric acid, $H.HgCl_3$ (p. 271). The acidity of an aqueous solution of mercuric chloride is neutralized by the addition of sodium chloride, which would indicate the formation of such salts. When ammonium hydroxide is added to its solution, a heavy white precipitate is produced. Its composition varies with the concentration, the temperature, and the quantities of mercuric chloride and ammonia. *White precipitate* (*Hydrargyrum præcipitatum album*) has the formula $HgClNH_2$. This compound may be regarded as mercuric chloride, in which one atom of chlorine is replaced by the amido-group, NH_2: $Hg\begin{smallmatrix}\diagup Cl\\ \diagdown NH_2\end{smallmatrix}$, and it has been called *amido-mercury chloride.* Or it may be derived from ammonium chloride by the substitution of a mercury atom for two hydrogen atoms, $NHgH_2Cl$, mercurammonium chloride. Similar mercuri- and mercuro-ammonium derivatives are numerous.

Mercuric Iodide, HgI_2 (*Hydrargyrum biiodatum*), is formed by the direct union of mercury with iodine. When potassium iodide is added to a solution of mercuric chloride, mercuric iodide separates as a yellow precipitate, which immediately becomes red. It is readily soluble in mercuric chloride and potassium iodide solutions; it crystallizes from alcohol in bright red quadratic pyramids. Upon heating dry mercuric iodide to 150°, it suddenly becomes yellow, and fuses at 223° to a red liquid; a portion subliming before this in yellow, shining, rhombic needles. On touching these with some solid, they become red, with separation of heat, and are changed into an aggregate of quadratic pyramids. Mercuric iodide is therefore dimorphous. It crystallizes (depending on the temperature), in either yellow or red forms, from methylene iodide, CH_2I_2, of which 100 parts dissolve 16.6 parts of mercuric iodide at 100°.

The great resistance shown by all the mercury halides toward concentrated sulphuric acid is noteworthy. Even in the heat the halogen is very slowly expelled. They are also very stable toward caustic soda and potash. This is in harmony with the tendency of mercury to yield derivatives which are only slightly dissociated.

Mercuric Cyanide, $Hg(CN)_2$, is obtained by dissolving yellow mercuric oxide in aqueous prussic acid or by heating Prussian blue with mercuric oxide and water. It crystallizes from water in white quadratic prisms. It is also soluble in alcohol and can be extracted from its aqueous solution by shaking with ether. It breaks down on heating into mercury and cyanogen gas (p. 236). The mercury and cyanogen group seem to be differently combined from other metals and cyanogen, *e. g.*, potassium cyanide. Mercuric cyanide has a very low degree of dissociation. Silver nitrate does not precipitate silver cyanide from its aqueous solution, nor does an alkaline hydroxide throw out mercuric oxide. Hydrogen sulphide and alkaline sulphides decompose it with formation of mercury sulphide and hydrocyanic acid or alkaline cyanide. Unlike potassium cyanide it is very stable toward acids.

Mercuric Oxide, HgO, is obtained by the prolonged heating of metallic mercury near the boiling point in the air, or by the ignition of mercurous or mercuric nitrate and mercury. It forms a red, crystalline powder (*Hydrargyrum oxydatum rubrum*), of specific gravity 11.2. When sodium hydroxide is added to a solution of mercuric chloride, mercuric oxide separates as a yellow, amorphous precipitate (*Hydr. oxyd. flavum via humida paratum*). Both modifications become black when heated, but change to a yellowish-red on cooling. Mercuric oxide decomposes into mercury and oxygen at about 400°.

Mercuric oxide combines directly with ammonia, to form the compound $2HgO.NH_3$, which explodes with violence when heated.

Mercuric Nitrate, $Hg(NO_3)_2$. It is difficult to obtain this salt pure, because it is inclined to form basic compounds. A solution of it may be made by dissolving mercury or mercuric oxide in an excess of hot nitric acid. On diluting the solution with water the basic salt, $Hg(NO_3)_2 . 2HgO + H_2O$, separates, and this may be converted into pure mercuric oxide by boiling with water.

Mercuric Sulphate, $HgSO_4$, is produced by digesting mercury or its oxide with an excess of concentrated sulphuric acid. It forms a white, crystalline, insoluble mass, which becomes yellow on heating. It yields the hydrate $HgSO_4 + H_2O$ with a little water, but much of the latter decomposes it into sulphuric acid and the yellow insoluble *basic* salt, $HgSO_4 . 2HgO$ (*Turpethum minerale,* Turpeth mineral).

Mercuric sulphate forms double salts with the alkaline sulphates, *e. g.*, $HgSO_4 . K_2SO_4 + 6H_2O$; these are isomorphous with the corresponding double salts of the magnesium group (p. 315).

Mercuric Sulphide, HgS, occurs in nature as *cinnabar,* in radiating crystalline masses, or in hexagonal prisms of dark-red color. It is obtained artificially by rubbing together mercury and flowers of sulphur with water, or it is produced as a black microcrystalline precipitate by the precipitation of a solution of a mercuric salt with hydrogen sulphide. If the black sulphide be heated with exclusion of air it sublimes as a dark-red mass of radiating crystalline structure, and is perfectly similar to natural cinnabar. A similar conversion of the black modification into the red is effected by continued heating of the same to 50° with a solution of potassium or ammonium sulphide. The red mercury sulphide thus obtained is employed as *artificial cinnabar* in painting.

The mercury compounds can be readily recognized by the following reactions. When heated with dry sodium carbonate in a small test-tube, mercury escapes, and condenses upon the side in metallic drops. Tin, copper and zinc throw out metallic mercury from its solutions. If a piece of sheet copper be dipped into the same, mercury is deposited as a gray coating, which on being rubbed acquires a metallic luster. When a dry mixture of a mercuric salt, lime and potassium iodide is heated yellow (or red) mercuric iodide sublimes. This is the only iodide not decomposed by caustic lime. The mercurous compounds are distinguished from the mercuric by their precipitation by hydrochloric acid.

The heats of formation of the chlorides of the seven metals of the second group are as follows:

$$(Mg,Cl_2) = 151$$

$$(Ca,Cl_2) = 170 \qquad (Zn,Cl_2) = 97$$
$$(Sr,Cl_2) = 185 \qquad (Cd,Cl_2) = 93$$
$$(Ba,Cl_2) = 195 \qquad (Hg,Cl_2) = 54.$$

The heats of formation in the first sub-class increase with the rise in the atomic weights, while the opposite is observed in the second sub-class. The heats of formation of other derivatives of the two groups manifest similar relations.

Comparing these numbers with the quantity of heat which is disengaged in the formation of aqueous hydrochloric acid:

$$\mathrm{H,Cl} = 22;\ \mathrm{H,Cl,Aq} = 39.3,$$

we find explained the behavior of the metals toward this acid. All metals liberating a greater quantity of heat than 39.3 Cal. in the formation of their chlorides (calculated for 1 equivalent of metal) are in condition to decompose the dilute acid. Most of the metals belong to this class; mercury, copper, silver, gold, lead, thallium, and some others, set free a less amount of heat, and hence are not able to decompose dilute hydrochloric acid.

The slight quantity of heat developed in the formation of hydrogen sulphide,

$$\mathrm{S,H_2} = 4.5,$$

indicates that the same is readily decomposed by all the metals. In the same way, by adding the heat of solution,

$$\mathrm{S,H_2,Aq} = 9.2,$$

we can easily ascertain which metals are precipitated by hydrogen sulphide from their chlorides, etc.

If in the thermo-chemical equation,

$$(\mathrm{Me,Cl_2,Aq}) + (\mathrm{S,H_2,Aq}) = (\mathrm{Me,S}) + 2(\mathrm{H,Cl,Aq}),$$

the sum of the heat developed upon the right side is greater than that upon the left, the reaction will occur (precipitation of metallic sulphides); in the opposite case the sulphide is decomposed by the dilute hydrochloric acid.

COPPER, SILVER, AND GOLD.

Considering the magnitude of their atomic weights, copper, silver, and gold, bear the same relation to the alkali group, especially to sodium, as zinc, cadmium, and mercury bear to magnesium:

Na = 23.05 Mg = 24.36
Cu = 63.6 Zn = 65.4
Ag = 107.93 Cd = 112
Au = 197.2 Hg = 200.3.

They occupy an entirely analogous position in the three great periods of the periodic system of the elements (p. 246), and constitute the transition from the elements of group VIII, especially from cobalt, palladium, and platinum, to the elements of group II—zinc, cadmium, and mercury:

Co = 59 Cu = 63.6 Zn = 65.4
Pd = 106 Ag = 107.93 Cd = 112
Pt = 194.8 Au = 197.2 Hg = 200.3.

This intermediate position of the three elements about to be discussed is clearly shown in their entire physical deportment. While the elements of group VIII, with the last members, cobalt, palladium, and platinum, fuse with difficulty and do not volatilize, copper, silver, and gold constitute the transition to the readily fusible and volatile elements, zinc, cadmium, and mercury. They take an intermediate position, too, with reference to their coefficients of expansion, their atomic volumes, and other physical properties. It is noteworthy that the ability to conduct heat and electricity attains its maximum in copper, silver, and gold.

Not only are the properties of the free elements determined by the position of the latter in the periodic system, but those of their derivatives, and especially such as depend upon the valence of the elements, are influenced to a marked degree by the above relation. In consequence of the double periodicity of the great periods, copper, silver, and gold attach themselves to group I, and especially to sodium, just as the elements immediately following, zinc, cadmium and mercury, arrange themselves with group II and magnesium. Hence we find copper, silver, and gold, like sodium, yielding compounds of the form $\overset{\mathrm{I}}{Me}X$, in which they appear univalent. Some of these are isomorphous, *e. g.*, silver sulphate, Ag_2SO_4, with sodium sulphate, Na_2SO_4; sodium chloride, NaCl, cuprous chloride, CuCl, and silver chloride, AgCl, crystallize in forms of the regular system.

But we may say that the similarity of copper, silver, and gold to sodium is confined to these few external properties. Just as the heavy metals, zinc, cadmium, and mercury differ in many properties from the light metal magnesium (p. 313), so do the metals copper, silver, and gold, possessing a high specific gravity, distinguish themselves in a still higher degree from the light metal sodium. They possess all the properties belonging to the heavy metals, which are mainly characterized by the insolubility of the oxides, sulphides, and many salts, so that they arrange themselves in a less marked degree with the alkali metals.

In the compounds constituted according to the form $\overset{\mathrm{I}}{Me}X$, in which copper, silver, and gold appear univalent, they exhibit great similarity. Thus, the chlorides, CuCl, AgCl, and AuCl, are white and insoluble in water; soluble, however, in concentrated hydrochloric acid, ammonia, the alkaline hyposulphites, etc., and form double chlorides, very similar to each other, with other chlorides. While silver only enters compounds of the form $\overset{\mathrm{I}}{Ag}X$, copper and gold are capable of yielding another form; copper forms, besides cuprous, $\overset{\mathrm{I}}{Cu}X$, also cupric, $\overset{\mathrm{II}}{Cu}X_2$, derivatives, in which it appears to be bivalent. The latter are much more stable than the former, and embrace the ordinary copper salts. Gold, however, besides furnishing aur*ous*, $\overset{\mathrm{I}}{Au}X$, compounds, has aur*ic* derivatives, $\overset{\mathrm{III}}{Au}X_3$, in which the metal appears to be trivalent (see the Thallium Group).

While copper and gold, in their lower forms, are analogous to silver (and in less degree, to sodium), the cupr*ic* derivatives show a great resemblance to the compounds of the metals of the magnesium group and other metals in their bivalent combinations. Thus, the sulphates of zinc, magnesium, cupric oxide (CuO), ferrous oxide (FeO), nickelous oxide (NiO), cobaltous oxide (CoO), and manganous oxide (MnO), are similarly constituted, resemble each other, are isomorphous, and form entirely analogous double salts (p. 315) with the alkaline sulphates. In the same way the carbonates ($\overset{\mathrm{II}}{Me}CO_3$), the chlorates and bromates ($\overset{\mathrm{II}}{Me}Cl_2O_6 + 6H_2O$) and others, are similarly constituted and isomorphous. In its aur*ic* derivatives, gold exhibits some similarity to the aluminium compounds ($\overset{III}{Al}X_3$), to those of indium ($\overset{III}{In}X_3$) and other metals, in their trivalent combinations. Here we see, as already observed with mercury (p. 321), that the *similarity of the compounds of the metals is influenced by the similarity of forms or types*, according to which they are composed, *i. e.*, by the valence of the metals. If a metal form several series of compounds of different types, each series is usually more or less similar to the compounds of other metals of like type. In this manner is shown the resemblance of the compounds of the following types:

Na_2O Sodium oxide.	Ag_2O Silver oxide.	Cu_2O Cuprous oxide.	Au_2O Aurous oxide.	Tl_2O Thallous oxide.
MgO Magnesium oxide.	ZnO Zinc oxide.	CuO Cupric oxide.	FeO Ferrous oxide.	HgO Mercuric oxide.
Al_2O_3 Aluminium oxide.	Fe_2O_3 Ferric oxide.	Au_2O_3 Auric oxide.	Tl_2O_3. Thallic oxide.	

The character of their derivatives, varying with the degree of combination or valence, becomes quite marked with chromium, manganese and iron, as we shall later see. The heavy metals also exhibit a strongly positive and basic character in their univalent combinations. Thus, silver oxide (Ag_2O) and thallous oxide (Tl_2O) are strong bases, forming neutral-reacting salts with acids, and even cuprous and aurous oxides are more strongly basic than their higher forms of oxidation. The metalloidal character of the metals and the acid nature of their oxides begin to appear in their trivalent combinations. Thus, in the hydroxyl derivatives of aluminium, indium, and gold, $Al(OH)_3$, $In(OH)_3$, $Au(OH)_3$, hydrogen may be replaced by the alkalies just as in boric acid, $B(OH)_3$. Their higher forms of oxidation show, like those of the metalloids, a pronounced acid-like character (as PbO_2, PtO_2, CrO_3, FeO_3) which is only lessened by a high atomic weight of the metal (as in PbO_2 and PtO_2).

The heats of formation of the copper, silver and gold compounds of the MeX type show the same gradation as those of the zinc group (p. 327):

$(Na, Cl) = 97.6$ $(Ag, Cl) = 29.3$
$(Cu, Cl) = 32.8$ $(Au, Cl) = 5.8$.

COPPER.

$Cu = 63.6$.

Native copper is found in large quantities in America (Lake Superior), China, Japan, also in Sweden and in the Urals. It frequently occurs crystallized in cubes and octahedra. The most important and most widely distributed of its ores are: cuprite (Cu_2O), malachite ($CuCO_3 . Cu(OH)_2$)

and azurite ($2CuCO_3 . Cu(OH)_2$) (basic carbonates), chalcocite (Cu_2S), and especially chalcopyrite ($Cu_2S . Fe_2S_3$) and bornite ($3Cu_2S . Fe_2S_3$).

Metallurgy of Copper.—The extraction of copper from its oxygen ores is very simple: metallic copper is melted out when the ores are ignited along with charcoal. The sulphur ores are more difficult to work. 1. The divided material is first roasted in the air, whereby the sulphur content is reduced:

$$3(Cu_2S . Fe_2S_3) + 21O = 6CuO + 5FeS + FeO + 7SO_2.$$

2. The mass is afterward fused, when we get the so-called *coarse metal*, which contains iron sulphide in addition to copper sulphide:

$$6CuO + 5FeS = (3Cu_2S + FeS) + 4FeO + SO_2.$$

3. Crude copper (black copper) is obtained by further roasting and by the "fusion reaction" of this mass:

$$3Cu_2S + FeS + 9O = 3Cu_2O + FeS + 3SO_2 = 3Cu_2 + FeO + 4SO_2.$$

The ferrous oxide formed here is taken up by the silica to form a slag. In the more recently constructed works, particularly in the United States, the sulphide ores are first roasted and then melted in cupola or reverberatory furnaces, after which the coarse metal is subjected to the Bessemer process and the resulting black copper is electrolyzed. See Chem. Zeit. 1895, 977; 1897, 995; also Jahrb. d. Chem. v (1895), 287.

In refining copper electrolytically, plates cast from black copper are suspended as anodes in the solution of copper sulphate. The kathodes are plates of pure copper. The copper is dissolved from off the anode and deposited on the kathode. Impurities, including any of the nobler metals, settle at the bottom as mud.

Copper can also be obtained in the wet way from its ores. The pulverized ore is treated with solutions of ferric chloride or sulphate, when the copper sulphide is transposed to soluble copper salts in the sense of the following equations:

$$\begin{gathered} Cu_2S + Fe_2Cl_6 = 2FeCl_2 + Cu_2Cl_2 + S; \\ CuS + Fe_2Cl_6 = CuCl_2 + 2FeCl_2 + S; \\ Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S. \end{gathered}$$

The copper is then precipitated electrolytically from the solution.

The following countries are rich in copper: United States (Lake Superior and Montana), Spain and Portugal, also Chili, Japan, and Germany (Prussia, Mansfield).

The following are excellent reference works on the metallurgy of copper: Ost's Technologie, Dammer's Technologie (p. 190), and Dürre's Vorlesungen über allgemeine Hüttenkunde (Halle, 1898).

To obtain chemically pure copper, the pure oxide is heated in a stream of hydrogen, or the solution of copper sulphate is decomposed by electrolysis.

Metallic copper possesses a characteristic red color, and transmits a green light in thin leaflets. It is rather soft and ductile, and possesses a specific gravity of 8.5–8.9. It melts at about 1080°, and vaporizes in the oxyhydrogen flame. It remains unaltered in dry air; in moist, it is gradually coated with a green layer of basic copper carbonate. When heated in the air, it oxidizes to black cupric oxide.

Copper is not changed by dilute hydrochloric or sulphuric acids; if it be moistened with these, and exposed to the air, it absorbs oxygen, and gradually dissolves. It is similarly dissolved by ammonium hydroxide. Hot concentrated sulphuric acid converts it into copper sulphate, with evolution of sulphur dioxide. It dissolves in dilute nitric acid in the cold, with evolution of nitric oxide. Zinc, iron and also phosphorus precipitate metallic copper from the aqueous solutions of its salts.

Copper forms two series of compounds, known as cupr*ous* and cupr*ic*. In the latter copper is bivalent:

$$CuO \qquad CuCl_2 \qquad Cu(OH)_2 \qquad CuSO_4.$$

These are more stable than the cupr*ous* derivatives; the ordinary copper salts belong to them. In many respects they resemble the compounds of other dyad metals, especially those of the magnesium group, and the *ous* compounds of iron (FeO), manganese (MnO), cobalt and nickel (see p. 329).

The cuprous compounds are, on the other hand, very unstable, absorb oxygen from the air, and pass into cupric derivatives. They show some similarity to the mercurous derivatives (p. 323), and possess an analogous composition:

$$CuCl \qquad CuI \qquad Cu_2O \qquad Cu_2S.$$

Oxygen salts of cuprous oxide are not known.

From the formulas given above, copper, like silver, is univalent in the cupr*ous* compounds. This is also experimentally indicated by the boiling and melting points shown by solutions of cuprous salts in pyridine, piperidine, and methyl sulphide. The salts are not dissociated in these solutions; they are non-conductors. From what has been said on p. 268 some of them probably have the simple formula, especially cuprous bromide, $CuBr$.

Other salts are disposed to appear as double molecules; the cyanide is only known as $Cu_2(CN)_2$. We can therefore assume, as was done in the case of the mercurous salts, the presence of a bivalent group of two metallic atoms:

$$CN{-}Cu{-}Cu{-}CN \qquad Cl{-}Cu{-}Cu{-}Cl.$$

The vapor density of cuprous chloride even at 1700° corresponds to the formula Cu_2Cl_2. Both formulas should be given equal value. [See pp. 322, 324, 339, and Werner, Z. f. anorg. Ch. 15 (1897) 1].

CUPROUS COMPOUNDS.

Cuprous Oxide, Cu_2O, occurs as cuprite crystallized in regular octahedra. It is obtained artificially by boiling a solution of copper sulphate and grape sugar with potassium hydroxide, when it separates as a crystalline, bright red powder. It does not change in the air, and is readily soluble in ammonium hydroxide. The solution absorbs oxygen, and while forming cupric oxide acquires a blue color. By the action of sulphuric and other oxygen acids, it forms cupric salts, half of the copper separating as metal:

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O.$$

The *hydroxide*, $Cu_2(OH)_2$, is precipitated by the alkalies as a yellow powder from hydrochloric acid solutions of cuprous chloride, Cu_2Cl_2. It oxidizes in the air to cupric hydroxide.

Cuprous Chloride, $CuCl$ or Cu_2Cl_2, is produced by the combustion of metallic copper in chlorine gas (together with cupric chloride, $CuCl_2$), upon conducting hydrochloric acid over copper at a low, red heat; by boiling the solution of cupric chloride with copper:

$$CuCl_2 + Cu = Cu_2Cl_2,$$

and by the action of many reducing substances upon cupric chloride. It is most conveniently made by passing sulphur dioxide through a concentrated solution of copper sulphate and sodium chloride, when it separates as a white, shining powder, consisting of small tetrahedra. It fuses at 430°, and distils at about 1000°; its vapor density at 1600–1700° corresponds to the formula Cu_2Cl_2. In moist air it rapidly becomes green, owing to oxygen absorption, and the formation of basic cupric chloride, $Cu{<}^{Cl}_{OH}$. It becomes black on exposure to light. Cuprous chloride is readily soluble in concentrated hydrochloric acid and in ammonium hydroxide; both solutions possess the characteristic property of absorbing carbon monoxide. Colorless leaflets separate from solutions saturated with the gas. Their composition seems to be $Cu_2Cl_2 + CO + 2H_2O$.

Cuprous Iodide, CuI or Cu_2I_2, is precipitated from soluble cupric salts by potassium iodide:

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2.$$

By extracting the co-precipitated iodine by means of ether it is obtained as a gray powder, insoluble in acids.

Cuprous Sulphide, Cu_2S, occurs as chalcocite crystallized in forms of the rhombic system. It is produced by burning copper in sulphur vapor, and by heating cupric sulphide in a current of hydrogen; after fusion it solidifies in crystals of the regular system. Combined with silver sulphide it constitutes the mineral stromeyerite, $\left.\begin{matrix}Cu\\Ag\end{matrix}\right\}S$ or $Cu_2S.Ag_2S$, isomorphous with chalcocite.

Copper Hydride, CuH or Cu_2H_2, belongs to the derivatives of univalent copper. If a solution of copper sulphate be digested with hypophosphorous acid, the hydride separates as a yellow amorphous precipitate which soon acquires a brown color. At 60° it decomposes into copper and hydrogen.

With hydrochloric acid it forms cuprous chloride:

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2.$$

(Compare Mylius and Fromm, Ber. **27** (1894), 1, 647.)

CUPRIC COMPOUNDS.

The cupric salts, when hydrous, are generally colored blue or green; they are colorless in the anhydrous condition.

Cupric Hydroxide, $Cu(OH)_2$, separates as a voluminous bluish precipitate when sodium or potassium hydroxide is added to soluble copper salts. When heated, even under water, and particularly in the presence of alkali, it loses water, and is changed to black cupric oxide. In the presence of alkaline chlorides, or of cupric chloride it is partly reduced to a cuprous salt with the production of an alkaline peroxide in the evolution of oxygen:

$$2Cu(OH)_2 + 2KBr = Cu_2Br_2 + K_2O_2 + 2H_2O.$$

(Spring and Lucion, Z. f. anorg. Ch. 2 (1892), 195).

Cupric Oxide, CuO, is usually obtained by the ignition of copper turnings in the air, or by heating cupric nitrate. It forms a black amorphous powder, which, at higher temperatures, settles together and acquires a metallic luster. By heating with organic substances their carbon is converted into carbon dioxide, and the hydrogen into water, the cupric oxide being reduced to metal; upon this rests the application of cupric oxide in the analysis of such compounds.

Copper oxide and hydroxide dissolve in ammonium hydroxide with a dark-blue color. The solution possesses the power of dissolving wood fiber (cotton-wool, linen, filter-paper, etc.)—*Schweizer's reagent.*

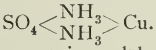
Cupric Chloride, $CuCl_2$, is formed by the solution of cupric oxide or carbonate in hydrochloric acid. It crystallizes from aqueous solution, with two molecules of water, in bright green rhombic needles, and is readily soluble in water and alcohol. When heated, it parts with its water, becoming anhydrous chloride, which at a red heat is decomposed into chlorine and cuprous chloride. It yields beautifully crystallized double salts with potassium and ammonium chlorides. Cupric bromide is like the chloride; the iodide is not known, since in its formation it at once breaks down into cuprous iodide and iodine.

Copper Sulphate, $CuSO_4 + 5H_2O$, cupric sulphate, copper vitriol—may be obtained by the solution of copper in concentrated sulphuric acid. It is produced on a large scale by roasting chalcocite. It forms large blue crystals of the triclinic system, which effloresce somewhat upon exposure. At 100° the salt loses four molecules of water; the fifth separates above 200°. The anhydrous sulphate is colorless, absorbs water very energetically, and returns to the blue hydrous compound.

Although copper sulphate only crystallizes with five molecules of water, it is capable, like the sulphates of the magnesium group, of forming double salts with potassium and ammonium sulphates, which crystallize with six molecules of water, and are isomorphous with the double salts of the metals of the magnesium group.

Copper sulphate is employed in electro-plating. When its solution is decomposed by the galvanic current copper separates at the negative pole, and deposits in a regular layer upon the conducting objects connected with the electrode. The positive pole is a copper plate: the ions, SO_4, dissolve a quantity of it equal to the copper deposited on the negative pole; hence the solution always has the same concentration.

Ammonium hydroxide added to a copper sulphate solution in sufficient quantity to dissolve the cupric hydroxide produced at first, changes the color of the liquid to a dark blue. From this solution alcohol precipitates a dark-blue crystalline mass with the composition $CuSO_4 . 4NH_3 + H_2O$. Heated to 150° this compound loses water and two molecules of ammonia, and becomes $CuSO_4 . 2NH_3$. It is supposed that these compounds are ammonium salts in which a part of the hydrogen is replaced by copper; they have been designated *cuprammonium compounds*, *e. g.*:



$$SO_4 < \begin{matrix} NH_3 \\ NH_3 \end{matrix} > Cu.$$

Cuprammonium sulphate.

The other soluble copper salts yield similar compounds with ammonium hydroxide.

Cupric Nitrate, $Cu(NO_3)_2$, crystallizes with three or six molecules of water, has a dark-blue color and is readily soluble in water and alcohol. Heat converts it into cupric oxide.

Copper Carbonates.—The neutral salt ($CuCO_3$) is not known. When sodium carbonate is added to a warm solution of a copper salt the basic carbonate, $CuCO_3 . Cu(OH)_2$, or $CO < \begin{matrix} O . Cu . OH \\ O . Cu . OH \end{matrix}$, separates as a green precipitate. It occurs in nature as *malachite*, which is especially abundant in Siberia. Another basic salt, $2CO_3Cu . Cu(OH)_2$, is the beautiful blue *azurite*.

Copper Arsenite separates as a beautiful bright green precipitate, upon the addition of sodium arsenite to a copper solution. This precipitate has never been obtained in homogeneous form and of a definite composition. It was formerly employed as a pigment, under the name of *Scheele's green*, but at present, owing to its poisonous character, it has been replaced by other green colors (Guignet's green and aniline green).

Cupric Sulphide, CuS, is a black compound, precipitated from copper solutions by hydrogen sulphide. It is insoluble in dilute acids. When moist, it slowly oxidizes in the air to cupric sulphate. Heated in a stream of hydrogen, it forms cuprous sulphide, Cu_2S.

Alloys of Copper.—Pure copper is very ductile, and may be readily rolled, and drawn out into a fine wire. It does not make good castings, because it contracts unequally upon cooling and does not fill out the moulds. For such purposes, alloys of copper are employed which, in addition, possess other technically valuable properties. The most important copper alloys are:

Brass, consisting of three parts of copper and one part of zinc. It has a yellow color, and is considerably harder than pure copper. Ordinarily, one or two per cent. of lead are added to the brass, which facilitates its working upon the turning-lathe. *Tombac* contains 15 per cent. of zinc, and has a gold-like color. The alloy of 1 part of zinc and 5.5 parts of copper answers for the manufacture of spurious gold leaf. The alloys of copper with tin are called *bronzes*. Most of the modern bronzes also contain zinc and lead; those from Japan, gold and silver. The *cannon bronze* contains 90 per cent. of copper and 10 per cent. of tin; bell-metal has 20–25 per cent. of tin.

Argentan is an alloy of copper, zinc, and nickel (see Nickel). The German copper coins consist of 95 per cent. of copper, 4 per cent. of tin, and 1 per cent. of zinc.

Of the more recently introduced alloys of copper we may mention:

Phosphor-bronze.—This consists of 90 parts of copper, 9 parts of tin and 0.5–0.8 parts of phosphorus. By the last ingredient the bronze is increased in hardness, and its solidity and resistance to oxidation are also increased. It is employed in making axle bearings and various parts of machinery.

Silicon bronze, containing silicon instead of phosphorus, is characterized by great firmness and conductivity. It is used for telephone wires and as conducting cables for electric railways.

Manganese bronze contains 70 per cent. of copper and 30 per cent. of manganese (it is the cupro-manganese of Létrange), and may be melted with copper and copper alloys, imparting to these solidity and great hardness. It is especially employed in making ship-propellers.

See page 347 for Aluminium Bronze.

Recognition of Copper Compounds.—Most copper compounds containing water have a blue or green color. With the exception of copper sulphide they all dissolve in ammonium hydroxide, with a blue color. Potassium ferrocyanide produces a reddish-brown precipitate or color in aqueous solutions of cupric salts. When a clean piece of iron is introduced into a copper solution, it becomes covered with a red layer of metallic copper. Volatile copper compounds tinge the flame blue or green. The spectrum of such a flame is characterized by several blue or green lines.

SILVER.

Ag = 107.93.

Silver occurs native. Its most important ores are argentite or silver glance (silver sulphide, Ag_2S) and various compounds with sulphur, arsenic, antimony, copper and other metals (light-red silver ore, proustite, Ag_3AsS_3, and dark-red silver ore, pyrargyrite, Ag_3SbS_3). Of rarer occurrence are combinations with chlorine (horn-silver, AgCl), bromine and iodine. Slight quantities of silver sulphide are present in almost every galenite (PbS). The principal localities for silver ores are the United States, Mexico, Bolivia, Australia, Saxony and Chili.

Metallurgy of Silver.—The metallurgy of silver ores involves methods dependent upon the silver content of the ore, the chemical constitution of the latter and the conditions of locality. It is usually a complicated procedure. The important methods alone will be indicated briefly here; details must be sought in special works upon chemical technology (p. 331). It is only the richest ores from which the silver can be directly recovered; most of the metal is obtained either (1) by first preparing an argentiferous lead and then separating these two metals subsequently; or (2) by the amalgamation process; or (3) by converting the silver into soluble compounds and precipitating it from the solutions.

1. The ores are worked together with lead ores for metal or, if they contain more than $\frac{1}{10}$ of silver, they are fused directly with lead. Various methods are pursued to enrich the silver-lead alloy with the first metal. (*a*) *Pattinsonizing.* When lead containing silver is fused and cooled slowly at first pure lead crystallizes out which is removed with sieves; an alloy rich in silver and readily fused remains. (*b*) *Parkes's process.* This method consists in adding zinc to the silver-lead alloy of low silver content and obtaining thereby an alloy of lead-zinc-silver, fusible with difficulty. When the fusion cools this alloy appears on the surface as "zinc crust." The zinc is expelled from it by distillation. The lead now rich in silver (obtained by one or the other method) is cupelled, *i. e.*, it is heated with air-access in a furnace the bottom of which consists of a porous mass. The lead is oxidized to lead oxide which partly escapes and is in part absorbed. The silver is not oxidized and remains in the cupel.

2. The amalgamation process is based on the fact that mercury dissolves silver and also decomposes its compounds with the formation of an amalgam.

The ore is roasted with sodium chloride, whereby silver chloride is produced. The divided material is then mixed with iron scraps and water in rotating vessels. The iron causes the precipitation of the metallic silver from its chloride:

$$2AgCl + Fe = FeCl_2 + 2Ag.$$

To free the metal from various impurities it is dissolved in mercury and the liquid amalgam ignited, when mercury distils off and silver remains. Owing to scarcity of combustible material, the conversion of silver ores into silver chloride is executed, in Mexico and Peru, by mixing the ores with sodium chloride and copper sulphate in the presence of water. In this way cuprous chloride is produced, which is transposed, with silver sulphide, into silver chloride and cuprous sulphide:

$$Cu_2Cl_2 + Ag_2S = Cu_2S + 2AgCl.$$

3. *By solution and precipitation.* The ores are roasted alone and afterwards together with salt. Silver sulphate is first produced and then silver chloride. The roasted mass is extracted with a concentrated salt solution which dissolves the silver chloride, and from this solution the silver metal is precipitated by metallic copper. The resulting cuprous chloride solution is acted upon with iron to recover the copper (Augustin). Or after roasting the ore alone silver sulphate is dissolved out with water and the solution treated with copper (Ziervogel). The silver can also be dissolved out by sodium copper thiosulphate, the metal being then precipitated by means of a calcium sulphydrate solution (Russell).

Commercial silver (work-silver) is not pure, but invariably contains copper and traces of other metals in greater or less quantity. To prepare chemically pure metal, the work-silver is dissolved in nitric acid, and from the solution of nitrates thus obtained hydrochloric acid precipitates the silver as chloride:

$$AgNO_3 + HCl = AgCl + HNO_3.$$

The latter is reduced by various methods; either by fusion with sodium carbonate, or by the action of zinc or iron in the presence of water:

$$2AgCl + Na_2CO_3 = 2NaCl + 2Ag + CO_2 + O.$$
$$2AgCl + Zn = ZnCl_2 + 2Ag.$$

Silver is a pure white, brilliant metal, of specific gravity 10.5. It is tolerably soft and very ductile, and can be drawn out to a fine wire. It crystallizes in regular octahedra. It fuses at 960°, and is converted into a greenish vapor in the oxyhydrogen flame. It is the best conductor of heat and electricity. Silver is not oxidized by oxygen; by the action of ozone it is covered with a very thin layer of silver peroxide. When in molten condition, silver absorbs 22 volumes of oxygen without combining chemically with it; the absorbed gas escapes again when the metal cools [sprouting or spitting of silver].

Silver is capable of existing in three allotropic forms, which have properties greatly different from those of ordinary silver. The first form is soluble in water and has a blue color. The second variety is insoluble, and somewhat resembles the first form. The third closely resembles gold in color and luster. These allotropic varieties of silver are broadly distinguished from normal silver by color. They very likely are more active conditions of silver, common silver being a polymerized variety (*Am. Jr. Science*, 37, 476).

Silver unites directly with the halogens; by the action of hydrochloric acid it becomes coated with an insoluble layer of silver chloride. Boiled with strong sulphuric acid, it dissolves to sulphate:

$$2Ag + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O.$$

The best solvent of silver is nitric acid, which even in a dilute state and unaided by heat, converts it into nitrate.

As silver is rather soft, it is usually employed in the arts alloyed with copper, whereby it acquires a greater hardness. Most silver coins consist of 90 per cent. of silver and 10 per cent. of copper; the English shillings contain 92.5 per cent. of silver. What is termed the *fineness* of silver is the number of parts per thousand which the alloy contains.

Oxygen forms three compounds with silver, but only the oxide yields corresponding salts.

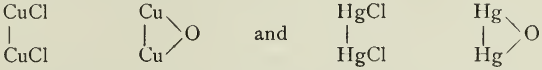
Silver Oxide, Ag_2O, is thrown out of a silver nitrate solution by sodium or potassium hydroxide as a dark-brown, amorphous precipitate. It is somewhat soluble in water, and blues red litmus-paper. In this, and in the neutral reaction of the nitrate, the strongly basic, alkaline nature of silver and its oxide exhibits itself; the soluble salts of nearly all of the other heavy metals show an acid reaction (p. 330). When heated to 250°, the oxide decomposes into metal and oxygen; at 100° it is reduced by hydrogen. Silver hydroxide, AgOH, is not known; the moist oxide reacts, however, very much like an hydroxide.

On dissolving precipitated silver oxide in ammonium hydroxide, black crystals ($Ag_2O.2NH_3$) separate when the solution evaporates, and when dry these explode upon the slightest disturbance—fulminating silver.

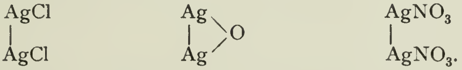
Silver Suboxide, Ag_4O, is said to be produced by heating silver citrate in a current of hydrogen, and is a black, very unstable powder, which decomposes readily into silver oxide and silver.

Silver Peroxide, AgO or Ag_2O_2, is formed by passing ozone over silver or its oxide, or by the decomposition of the nitrate by the electric current. It consists of black, shining octahedra, and at 100° decomposes into silver oxide and oxygen (Mulder).

The salts of silver correspond to the oxide Ag_2O, and are all constituted according to the form AgX, hence are termed argentic. They are analogous to the cuprous and mercurous derivatives, and show a great resemblance to the former. It would, therefore, be more correct to designate them argent*ous*. Compounds of the bivalent form AgX_2 are not known for silver. If, however, the mercurous and cuprous compounds are expressed by double formulas (pp. 322, 332):



which view is supported by their chemical deportment, and is experimentally confirmed in the case of cuprous chloride by its vapor density; those of silver might be represented by analogous formulas:



Then the silver atom would be bivalent and a complete parallelism would be established with copper. In support of this view there exists the fact that when the silver halides are dissolved in pyridine, methyl sulphide, etc., the colligative properties of their solvents are influenced as if halide molecules possessing the formulas Ag_2Cl_2, Ag_2Br_2, Ag_2I_2, and possibly in part higher formulas, were present. See pp. 268, 332. The chemical formulas of solid bodies do not generally designate their true molecular values as in the case of gases, but only their simplest atomic composition. It is very probable that even the simplest chemical compounds, *e. g.*, potassium chloride and silver chloride, consist in their solid condition of complex molecules corresponding to the formulas $(KCl)_n$, $(AgCl)_m$. An argument supporting this view is afforded by the existence of different modifications of chloride and bromide of silver; these differ from each other in their external properties, and their varying susceptibilities to light. The doubling of formulas, as shown above with Cu_2Cl_2, Hg_2Cl_2, etc., is mainly due to the tendency to deduce all the compounds of an element from a constant value, according to the doctrine of constant valence. This is, however, impossible (p. 169, 322). According to present notions of valence, and as it is presented in the periodic system, compounds (MeCl, $MeCl_2$, $MeCl_3$, etc.) are constituted according to definite forms or types that may materially determine their properties (p. 322). So far as the similarity of metallic compounds is concerned, it is of secondary importance whether the quantities corresponding to the simple formulas, in the solid or gaseous state, do unite to larger, complex molecules (compare HgCl and Cu_2Cl_2,—$AlCl_3$, $Al(CH_3)_3$ and Al_2Cl_6, $GaCl_3$ and Ga_2Cl_6,—$SnCl_2$, Sn_2Cl_4, $PbCl_2$, etc.). In case of the sesquioxides Me_2O_3 it is also immaterial whether they are derived from supposed trivalent elements, or from those that are quadrivalent. The same may be remarked of the metallic compounds $Me_3O_4 = (MeO.O)_2Me$ (see Spinels, 351).

The use of simple or of double formulas for the metallic compounds is therefore of no special importance.

Silver Chloride, AgCl, exists in nature as horn-silver. When hydrochloric acid is added to solutions of silver salts, a white, curdy precipitate separates; the same fuses at 490° to a yellow liquid, which solidifies to a horn-like mass. The chloride is insoluble in dilute acids; it dissolves somewhat in concentrated hydrochloric acid and in sodium chloride, very easily in ammonium hydroxide, potassium cyanide, and sodium hyposulphite. It crystallizes from ammoniacal solutions in large, regular octahedra. Dry silver chloride absorbs ammonia gas, forming a white compound of the formula $2AgCl.3NH_3$, which at 38° gives up its ammonia.

Silver Bromide, AgBr, is precipitated from silver salts by hydrobromic acid or soluble bromides. It has a bright yellow color and dissolves with more difficulty than the chloride in ammonium hydroxide; in other respects it is perfectly similar to the latter. Heated in chlorine gas it is converted into silver chloride.

Silver Iodide, AgI, is distinguished from the chloride and bromide by its yellow color, and its insolubility in ammonia. Fused silver iodide at first solidifies in isometric crystals, which gradually change to hexagonal forms, but when the latter are heated to 146°, they suddenly revert to the isometric forms. It dissolves readily in hydriodic acid, to AgI.HI, which, upon evaporation of the solution, separates in shining scales. Heated in chlorine or bromine gas, it is converted into chloride or bromide; conversely, chloride and bromide of silver are converted into silver iodide by the action of hydriodic acid.

These opposite reactions are explained by the principle of the greatest evolution of heat. Chlorine and bromine expel iodine from all iodides because the heat of formation of the latter is less than that of the bromides and chlorides. Again, hydriodic acid (gaseous or in aqueous solution) converts silver chloride into the iodide according to the equation:

$$AgCl + HI = AgI + HCl,$$

because the heat modulus of the reaction is positive (for gaseous halogen hydrides +12.5 Cal., for the solution +10.6 Cal. See the Table at close of book). Yet it may be noted here that Julius found that silver chloride and iodide were changed to bromide upon heating them in bromine vapor, and further that the chloride and bromide were also changed by iodine vapor into silver iodide. This is evidently an example of mass action [Z. f. anal. Ch. (1883) **22**, 523; also Blau, Monatsheft **17** (1896), 547].

Sunlight, and also other chemically active rays (magnesium light, phosphorus light) color silver chloride, bromide, and iodide at first violet, then gray-black, whereby they are probably converted into compounds of the form Ag_2X. Pure silver iodide is rather non-sensitive to light, but exceedingly sensitive if it contains silver nitrate or substances which can take it up (*e.g.* tannin); on this depends the application of these salts in photography.

When silver plates, previously exposed to iodine, bromine or chlorine vapors, and consequently covered with a thin layer of a silver halide, are placed in a *camera obscura* invisible images are produced. Mercury vapors condense on the spots which were exposed to the light and visible pictures appear (Daguerreotype, 1839). This was the first photographic process but it has been replaced by others: (1) *Wet collodion process.* A glass plate is covered with collodion (a solution of pyroxylin in an ethereal solution of alcohol) holding in solution cadmium iodide and ammonium iodide together with about one-fourth part of ammonium bromide. After the evaporation of the ether the glass plate is immersed in a solution of silver nitrate, whereby silver iodide and bromide are precipitated upon the surface. The plate thus prepared is exposed to light in the *camera obscura*, and, after the action, dipped into a solution of pyrogallic acid or ferrous sulphate. These reducing substances separate metallic silver in a finely divided state, which is precipitated upon the places where the light has acted and the picture, before invisible, is "developed." The plate is now introduced into a solution of potassium cyanide or sodium hyposulphite, which dissolves the silver salts not affected by the light, while the metallic unaltered silver remains (fixing). (2) *Bromide-gelatine process.* The plates are coated with silver bromide, finely distributed in the molten gelatine. When the layers have solidified the dry plates can be preserved for a long time. The action of the light produces silver sub-bromide which is more rapidly reduced by alkaline pyrogallol, hydroquinone, hydroxylamine, by potassium ferrous oxalate and eikonogen (amido-β-naphthol-β-monosulphonate of sodium) than unaltered silver bromide, which in this case is also removed by sodium hyposulphite. The negative thus formed is covered at the places upon which the light shone by a dark layer of silver, while the places corresponding to shadows of the received image are transparent. The copying of the glass negative on paper sensitized with silver nitrate is executed in a similar manner.

Silver Nitrate, $AgNO_3$ (*Argentum nitricum*), is obtained by dissolving pure silver in dilute nitric acid, and crystallizes from its aqueous solution in large rhombic tables, isomorphous with potassium saltpeter. At ordinary temperatures it is soluble in one-half part of water or in four parts of alcohol, the solution has a neutral reaction, and in this respect differs from the salts of almost all metals, which react acid (p. 330). It fuses at 200°, and solidifies to a crystalline mass. When perfectly pure it is not affected by light. Organic substances turn it black. Silver nitrate is employed for cauterizing wounds (*lunar caustic*).

By dissolving work-silver in nitric acid a mixture of silver and copper nitrates is obtained. To separate the silver salt from such a mixture it is heated to redness, the copper being thus converted into oxide and the unaltered silver nitrate extracted with water.

Silver Nitrite, $AgNO_2$, is precipitated from concentrated silver nitrate solutions by potassium nitrite. It crystallizes in needles, dissolves with difficulty in water, and decomposes above 90°.

Silver Sulphate, Ag_2SO_4, is obtained by the solution of silver in hot sulphuric acid, and crystallizes in small rhombic prisms which are difficultly soluble in water. It is isomorphous with anhydrous sodium sulphate.

Silver Sulphite, Ag_2SO_3, is precipitated as a white, curdy mass, if sulphurous acid be added to the solution of the nitrate. It blackens in the light and decomposes at 100°:

$$2Ag_2SO_3 = Ag_2SO_4 + Ag_2 + SO_2.$$

Silver Nitride, AgN_3, is very similar to silver chloride. It is more stable towards light and when heated or struck explodes with great violence. Angeli claims that it can be readily obtained by adding a saturated aqueous solution of hydrazine sulphate to a concentrated aqueous solution of silver nitrite (Ber. 26 (1893) III, 885; see pp. 132, 324).

Silver Sulphide, Ag_2S, occurs in regular octahedra, as argentite. Hydrogen sulphide precipitates it as a black amorphous sulphide from silver solutions. By careful ignition in the air it is oxidized to silver sulphate. It is insoluble in water and ammonium hydroxide.

Silver Disulphide, Ag_2S_2, is a dark-brown amorphous powder. It is produced on mixing a solution of silver nitrate in benzonitrile with one of sulphur in carbon bisulphide. Dilute hydrochloric acid converts it into a mixture of sulphur and silver chloride, with evolution of hydrogen sulphide:

$$Ag_2S_2 + 2HCl = 2AgCl + H_2S + S.$$

Silvering.—When silver contains more than 15 per cent. of copper it has a yellowish color. To impart a pure white color to objects made of such silver they are heated to redness with access of air. The copper is thus superficially oxidized, and may be removed by dilute sulphuric acid. The surface of pure silver is then polished.

The silvering of metals and alloys (German silver, argentan) is executed in a dry or wet way. In the first, the objects to be silvered are coated with liquid silver amalgam, with a brush, and then heated in an oven; the mercury is volatilized, and the silver surface then polished.

At present, the galvanic process has almost completely superseded the other processes. It depends on the electrolysis of the solution of the double cyanide of silver and potassium (AgCN . KCN), whereby the silver is thrown out at the electro-negative pole and deposits upon the metallic surface in connection with that electrode.

To silver glass, cover it with a mixture of an ammoniacal silver solution, with reducing organic substances like aldehyde, milk-sugar, and tartaric acid. Under definite conditions, the reduced silver deposits upon the glass as a regular metallic mirror.

Recognition of Silver Compounds.—Hydrochloric acid throws down a white, curdy precipitate of silver chloride, which dissolves readily in ammonium hydroxide. Zinc, iron, copper, and mercury throw out metallic silver from solutions of silver salts, and from many insoluble compounds, like the chloride.

GOLD.

Au = 197.2.

Gold (*aurum*) usually occurs in the native state, and is found disseminated in veins in some of the oldest rocks. Gold sands are formed by the breaking and disintegration of these. It occurs, in slight quantity, in the sand of almost every river. Combined with tellurium it forms sylvanite, found in Transylvania and California. It is present in minute quantity in most varieties of pyrites and in many lead ores. For the separation of the gold grains the sand or pulverized rocks are washed with running water, which removes the lighter particles and leaves the specifically heavier gold.

The method of MacArthur and Forrest has of late found extensive application in the extraction of gold from its ores. The latter after reduction to a coarse powder and roasting are extracted with potassium cyanide solution. The gold dissolves as potassium aurocyanide and is precipitated with metallic zinc:

$$2Au + 4KCN + H_2O + O = 2KAu(CN)_2 + 2KHO.$$

The following localities are important gold producers: United States, Australia, Russia, South Africa, and the Klondyke in Alaska.

Native gold almost invariably contains silver, copper, and various other metals. To remove these, the gold is boiled with nitric or concentrated sulphuric acid. The removal of the silver by the latter acid is only complete if that metal predominates; in the reverse case a portion of it will remain with the gold. Therefore, to separate pure gold from alloys poor in silver they must first be fused with about three-fourths their weight of the latter metal. Gold may be separated from copper and lead by cupellation (p. 337).

Pure gold is rather soft (almost like lead) and has a specific gravity of 19 32. It is the most ductile of all metals, and may be drawn out into extremely fine wire and beaten into thin leaves, which transmit green light. At about 1060° it melts to a greenish liquid. It is not altered by oxygen, even upon ignition; acids do not attack it. It is only in a mixture of nitric and hydrochloric acids (aqua regia), which yields free chlorine, that it dissolves to gold chloride, $AuCl_3$. Free chlorine produces the same. Most metals, and many reducing agents (ferrous sulphate, oxalic acid) precipitate gold from its solution as a dark-brown powder.

As gold is very soft it wears away rapidly, and is, therefore, in its practical applications, usually alloyed with silver or copper, which have greater hardness. The alloys with copper have a reddish color, those with silver are paler than pure gold. The German, French, and American gold coins contain 90 per cent. of gold and 10 per cent. of copper. A 14-karat gold is generally employed for ornamental objects; this contains about 58.3 per cent. of pure gold (24 karats representing pure gold).

Gold, according to its atomic weight, belongs to the group of copper and silver; and, on the other hand, forms the transition from platinum to mercury. Its character is determined to a high degree by these double relations (p. 328). Like the other elements of high atomic weight, mercury, thallium, lead, and bismuth, belonging to the same series of the periodic system, it varies considerably in character from its lower analogues.

Gold, like silver and copper, yields compounds of the form AuX, aurous, analogous to the cuprous and argentous. Besides, it has those of the form AuX_3, auric derivatives, in which it is trivalent. These show the typical character of the trivalent combination form, which expresses itself in the acidity of the hydroxides (p. 330); auric hydroxide, $Au(OH)_3$, unites almost solely with bases. On the other hand, they show many similarities to the highest combination forms of the metals with high atomic weight: platinum (PtX_4), mercury (HgX_2), thallium (TlX_3), and lead (PbX_4) (p. 357).

AUROUS COMPOUNDS.

Aurous Chloride, AuCl, is produced by heating auric chloride, $AuCl_3$, to 180°, and forms a white powder insoluble in water. When ignited, it decomposes into gold and chlorine; cold water decomposes it slowly, more quickly on heating with formation of auric chloride and gold.

Aurous Iodide, AuI, separates as a yellow powder, if potassium iodide be added to a solution of auric chloride:

$$AuCl_3 + 3KI = AuI + I_2 + 3KCl.$$

When heated it breaks up into gold and iodine.

When auric oxide or sulphide is dissolved in potassium cyanide, large colorless prisms of the double cyanide, $AuCN.KCN$, crystallize out upon evaporation. The galvanic current and many metals precipitate gold from this compound; hence it serves for the separation of gold from ores and for electrolytic gilding, which, at present, has almost entirely superseded the gilding in the dry way (see p. 342).

Aurous Oxide, Au_2O, is formed by the action of potassium hydroxide upon aurous chloride. It is a dark-violet powder which at 250° decomposes into gold and oxygen. It is changed to auric chloride and gold by the action of hydrochloric acid.

Only a few double salts of the oxygen derivatives of univalent gold are known.

AURIC COMPOUNDS.

Auric Chloride, $AuCl_3$, results from the action of chlorine upon the metal. It is a lemon-yellow deliquescent mass, which dissolves readily in alcohol and in ether. On evaporating the solution long, yellow-colored needles of the composition $HAuCl_4.4H_2O$, hydrochlor-auric acid, remain. It forms beautifully crystallized double salts with many metallic chlorides, *e. g.*, $KAuCl_4 + 2H_2O$ and $NH_4AuCl_4 + 2\frac{1}{2}H_2O$. When a solution of auric chloride is heated with magnesium oxide a brown precipitate is obtained, from which all the magnesia is removed by concentrated nitric acid, leaving **Auric Oxide** (Au_2O_3). This is a brown powder which decomposes, near 250°, into gold and oxygen. If the precipitate containing the magnesia be treated, not with concentrated, but with dilute nitric acid, **Auric Hydroxide,** $Au(OH)_3$, remains as a yellowish-red powder. Both the oxide and hydroxide are insoluble in water and acids; they possess, however, acid properties, and dissolve in alkalies. Therefore the hydroxide is also called *auric acid*. Its salts, the aurates, are constituted according to the formula $\overset{\text{I}}{Me}AuO_2$, and are derived from the meta-acid, $HAuO_2 = AuO.OH$.

Potassium Aurate, $KAuO_2 + 3H_2O$, crystallizes in bright yellow needles, from a potassium hydroxide solution of auric oxide. These are readily soluble in water; the solution reacts alkaline. The corresponding aurates are precipitated from this solution by many metallic salts, *e. g.:*

$$KAuO_2 + AgNO_3 = AgAuO_2 + KNO_3.$$

The precipitate produced by magnesia in a solution of auric chloride (see above) consists of magnesium aurate, $Mg(AuO_2)_2$. Oxygen salts of auric oxide are not known.

Auric Sulphide, Au_2S_3, is precipitated as a blackish-brown compound, from gold solutions, by hydrogen sulphide. Its composition is either Au_2S_3 or Au_2S_2 (mixed with sulphur), depending on the conditions prevailing at the time. It dissolves in alkaline sulphides with formation of sulpho-salts, which are only derived from Au_2S (*e. g.*, K_3AuS_2). Hydrogen sulphide precipitates aurous sulphide, Au_2S, from hot gold solutions. It is steel-gray in color, and soluble in pure water, from which hydrochloric acid precipitates it. It is used in gold plating.

Stannous chloride ($SnCl_2$) added to an auric chloride solution produces, under certain conditions, a purple-brown precipitate, *purple of Cassius*, which is employed in glass and porcelain painting. Alumina and magnesia yield similar purples, and it appears that their red coloration is due to finely divided metallic gold.

On pouring ammonium hydroxide over auric oxide a brown compound is produced—*fulminating gold.* When this is dried and heated or struck it explodes very violently.

METALS OF GROUP III.

The trivalent elements, affording derivatives mainly of the form MeX_3, belong to group III of the periodic system (p. 246):

Sc = 44.1 Y = 89 La = 138 Yb = 173
B = 11 Al = 27.1
Ga = 70 In = 114 . . . Tl = 203.7.

These bear the same relation to one another as do the elements of group II (p. 299). Boron has the lowest atomic weight, and the basic, metallic character in it is reduced very much or does not appear at all. In its exclusively acidic hydroxide, $B(OH)_3$, it approaches the metalloids, and is therefore treated with them (p. 241).

Aluminium is a perfect metal; its hydroxide, $Al(OH)_3$, exhibits a predominating basic character, and yields salts with acids. Its relations to boron are like those of silicon to carbon, or of magnesium to beryllium. The connection of aluminium and boron with the same group plainly shows itself in the entire character of the free elements, and in their compounds. Thus aluminium and boron are not dissolved by nitric acid, but by boiling alkalies:

$$Al + 3KOH = Al(OK)_3 + 3H.$$

There is only a gradual difference between their hydrates. Boron hydroxide, $B(OH)_3$, not only acts as a feeble acid, but we also find that aluminium hydroxide manifests an acidic character, inasmuch as it is capable (pp. 258, 330) of forming metallic salts with strong bases (chiefly the alkalies); but owing to the higher atomic weight of aluminium the basic character exceeds the acidic.

Scandium, yttrium, lanthanum and ytterbium attach themselves to aluminium as the *first sub-group.* These constitute the third members of the great periods, and hence exhibit a pronounced basic character. As light metals, they are very similar to aluminium in their compounds, so that they are all embraced in one group, which (corresponding to the earthy nature of their oxides) is designated the *group of earth metals.* Cerium, praseodymium and neodymium bear a peculiar relation to lanthanum; their atomic weights are nearly alike and their properties very similar. They, like erbium, terbium, thulium, holmium and samarium, are by no means so accurately known that they can be assigned definite places in the periodic system. Most of them are probably mixtures of unknown elements.

The *second sub group* is more distinctly characterized and accurately investigated; it consists of the heavy metals, gallium, indium and thallium. These belong to the right side of the great periods, possess, therefore, a less basic character, and bear the same relation to one another as zinc, cadmium and mercury.

I. GROUP OF THE EARTH METALS.

ALUMINIUM.

Al = 27.1.

Aluminium, both in quantity and distribution, is one of the most important constituents of the earth's crust. As oxide, it crystallizes as ruby, sapphire and corundum; less pure as emery. It is commonly found as aluminium silicate (clay, kaolin), and in combination with other silicates, as feldspar, mica, and also in most crystalline rocks. It occurs, too, united with fluorine and sodium, as cryolite, $AlFl_3 . 3NaFl$, in large deposits, in Greenland.

Metallic aluminium is at present obtained almost exclusively by the electrolysis of alumina dissolved in fused cryolite. The oxygen burns the carbon anode to carbon monoxide and aluminium separates in the molten condition.

Metallic aluminium was first obtained as a gray powder by Wöhler in 1827 when he heated the chloride with potassium. Later he conducted the vapors of aluminium chloride over heated sodium or potassium, obtaining thereby globules of the metal. Bunsen, 1854, reduced the double chloride of sodium and aluminium with the electric current and separated aluminium also in powder form. St. Claire-Deville announced similar methods almost simultaneously. It is due to his efforts that the metal was produced on a commercial scale (1856). This he accomplished by reducing aluminium sodium chloride, partly with introduction of cryolite, by means of sodium:

$$AlCl_3 . NaCl + 3Na = 4NaCl + Al.$$

However, in 1888 this method was in use in but one factory. A new impulse was given to the manufacture of the metal after the discovery of Castner's and of Netto's methods of preparing metallic sodium. Equal parts of cryolite and sodium chloride were fused together and blocks of sodium of 5–7 kilograms in weight were dipped into the then molten mass, the slag, separated from the aluminium and containing sodium fluoride, was treated with aluminium sulphate and artificial cryolite prepared. This sodium method was abandoned as a consequence of the development of electrolysis. In America natural gas is used for heat and power purposes; and the power of Niagara Falls was turned to the production of electric currents. A portion of the Rhine Falls at Schaffhausen in Switzerland is applied to the same purpose. Another large aluminium plant exists at Froges near Grénoble. The electrolysis is conducted in accordance with the method of Héroult, using a solution of alumina in fused cryolite and fluorspar. The oxide breaks down quite readily into aluminium and oxygen. The Hall method, so largely used in America, is practically the same. (Compare Cl. Winkler, Ch. Zt., 1892, 349, and Elbs; *ibid.*, 1894, 1637; 1897, 995; especially W. Borcher's Elektrometallurgie, 1896, and his Elektrische Schmelzöfen, Halle, 1897.)

Aluminium is an almost silver-white metal of strong luster, very ductile, and it may be drawn out into fine wire and beaten into thin leaflets. Its specific gravity is 2.583; it belongs, consequently, to the light metals (see pp. 252, 313). It fuses at 660° but will not vaporize. It changes very little in the air at ordinary temperatures, and even when heated. If, however, thin leaves be heated in a stream of oxygen, they will burn with a bright light. Pure aluminium is attacked with difficulty by water. The commercial article, containing sodium, is more readily affected, while the amalgamated product is very easily and quickly acted upon by the reagent. Nitric acid affects aluminium only superficially; sulphuric acid dissolves it on boiling, while it is readily soluble, even in the cold, in hydrochloric acid, and in a solution containing 5 per cent. of acetic acid and some sodium chloride it is attacked at once. It dissolves in potassium and sodium hydroxide with evolution of hydrogen, and forms aluminates:

$$Al + 3KOH = K_3\,AlO_3 + 3H.$$

Owing to its stability in the air and beautiful luster, aluminium is sometimes employed for vessels and ornaments.

It has been found that vessels of aluminium are attacked by most foods and drinks. The effect is slight and diminishes rapidly with continual use. The relish of foods prepared in such vessels appears to suffer nothing by continuance nor does there appear to be any harmful influences to the general health (Plagge).

Alloys of copper with 5–12 per cent. of aluminium are distinguished by their great hardness and durability. They make good castings, and possess a gold-like color and luster. Under the name of aluminium bronze, they are used for the composition of various articles, as watches, spoons, etc. Their firmness and elasticity render them suitable for physical instruments (arms of balances) and watch springs.

Aluminium has a most remarkable affinity for oxygen. It has consequently been in use for quite a while in isolating other elements from their oxides (p. 136). Magnesium oxide is the only oxide not reduced by metallic aluminium. Alumina (corundum) always results in such reductions:

$$Cr_2O_3 + 2Al = Al_2O_3 + Cr_2.$$

When metallic oxides are heated with aluminium powder so much heat is liberated that violent explosions take place. H. Goldschmidt has recently discovered a means of controlling these rearrangements and of utilizing the immense heat of the reaction by igniting the mixture of metallic oxide and aluminium powder within by means of a percussion point at but one place and letting the transpositions advance from there. The "percussion point" consists of a magnesium band supplied at its end with a mixture of aluminium powder and barium peroxide or some other substance rich in oxygen. In such reactions the aluminium is converted into a slag of fused corundum, which on cooling crystallizes in part like the natural product.

Sulphides instead of oxides, can be used; this is sometimes advantageous because aluminium sulphide melts easily and can be readily separated from metals:

$$3CuS + 2Al = Al_2S_3 + 3Cu.$$

[See H. Goldschmidt, Ann. Chem. (1898) 301, 19.]

The heat evolved in the formation of aluminium hydroxide is 388.8 Cal. This far exceeds that of any other oxides:

$$Cu,O = 37; \; Fe_2,O_3,3H_2O = 191.$$

The heat corresponding to one atom of oxygen, is, therefore, 129.6 Cal.; since that of water is far less ($H_2,O = 69.0$), it must be decomposed by aluminium, with liberation of hydrogen (p. 273). If this does not transpire under ordinary conditions, the reason must be sought for in the insolubility of aluminium hydroxide. Indeed, the reaction occurs if aluminium chloride, or another salt, in which the aluminium oxide is soluble, be added to the water. Conversely, the high heat of formation of aluminium oxide explains why it is not reduced by carbon.

Aluminium unites in but one proportion with oxygen, Al_2O_3; this is the source of salts of the type AlX_3 (p. 349). Water decomposes them hydrolytically in part and that explains the acid reaction of their aqueous solutions; they have a sweet, acrid taste.

The trivalence of aluminium is shown in its organic derivatives, *e. g.*:

$$Al(CH_3)_3, \; Al(C_2H_5)_3, \text{ etc.}$$

Such compounds like those with hydrogen are best adapted for the determination of the valence of an element (p. 247). At sufficiently high temperatures the density of the vapors of aluminium chloride correspond to the formula $AlCl_3$, but at lower temperatures this, like other metallic chlorides (*e. g.*, tin dichloride, gallium chloride, etc., p. 339), shows a tendency to form larger molecules—to polymerize.

Aluminium Chloride, $AlCl_3$, is produced by the action of chlorine upon heated aluminium; also by heating a mixture of aluminium oxide and carbon in a current of chlorine:

$$Al_2O_3 + 3C + 6Cl = 2AlCl_3 + 3CO.$$

Chlorine and carbon do not act separately upon the oxide; by their mutual action, however, the reaction occurs in consequence of the affinity of carbon for oxygen, and of chlorine for aluminium. The oxides of boron and silicon show a similar deportment.

In order to get chloride free from iron and oxychloride, it is advisable to heat the metal in dry hydrochloric acid gas (Seubert and Pollard, Ber. (1891) 24, 2575).

Aluminium chloride may be obtained in white, hexagonal leaflets by sublimation. It sublimes readily, but will only fuse when subjected to high pressure (in a sealed tube) and at 193–194°. At 175–179° the fused, cooling mass exhibits the phenomenon of boiling and subliming (p. 229). The boiling point under the ordinary pressure is 183°.

Deville and Troost (1857) first determined the vapor density of aluminium chloride, bromide, and iodide at 440°, and found it to correspond to the formulas Al_2Cl_6, Al_2Br_6, and Al_2I_6. Later, Friedel and Crafts redetermined that of the chloride at 218–440° with like results. This led to the supposition that aluminium was quadrivalent in all its compounds (Jahresb. f. Ch. 1888, I, 131). The most recent investigations of Nilson and Peterson (Z. f. phys. Ch. I (1887), 459) have shown that at higher temperatures (above 760°) the vapor density of the chloride corresponds to the formula $AlCl_3$ (p. 339).

Aluminium chloride absorbs moisture from the air, and deliquesces. It crystallizes from a concentrated hydrochloric acid solution, with six molecules of water. On evaporating the aqueous solution, the chloride decomposes into aluminium oxide or hydroxide and hydrogen chloride:

$$2AlCl_3 + 3H_2O = Al_2O_3 + 6HCl.$$

It forms double chlorides with many metallic chlorides, viz.: $AlCl_3.NaCl$, $AlCl_3.KCl$. The solutions of these may be evaporated to dryness without decomposition. It also unites with many halogen derivatives of the metalloids:

$$AlCl_3.PCl_5, \qquad AlCl_3.POCl_3, \qquad AlCl_3.SCl_4.$$

Aluminium Bromide, $AlBr_3$, is obtained like the chloride, and consists of shining leaflets which fuse at 90° and boil at 265–270°.

Aluminium Iodide, AlI_3, is formed on heating aluminium filings with iodine. It is a white, crystalline mass, fusing at 185°, and boiling at 360°. It is best prepared by covering sheet aluminium with carbon bisulphide, and then adding the calculated amount of iodine gradually, letting the whole stand for some time, and then distilling off the carbon bisulphide. The reaction occurring between aluminium iodide and oxygen is interesting. If the vapor of the former be mixed with the latter, and then brought in contact with a flame, or if acted upon by an electric spark, a violent detonation will ensue; aluminium oxide and iodine result:

$$2AlI_3 + 3O = Al_2O_3 + 3I_2.$$

This deportment is due to the great difference in the heats of formation of the aluminium oxide (about 380 Cal.), and the iodide (140.6 Cal.). The chloride and bromide are similarly decomposed, but with less violence.

Aluminium Fluoride, $AlFl_3$, obtained by conducting hydrogen fluoride over heated aluminium oxide or hydroxide, sublimes at a red heat in colorless rhombohedra. It is insoluble in water, unaltered by acids, and is very stable. It yields insoluble double fluorides with alkaline fluorides. The compound, $AlFl_3.3NaFl$, occurs in Greenland, in large deposits, as cryolite, and is employed in the soda and alumina manufacture (p. 292).

Aluminium Oxide, Al_2O_3, is found crystallized in hexagonal prisms in nature, as ruby, sapphire, and corundum, colored by other admixtures. Impure corundum, containing aluminium and iron oxides, is called emery, and serves for polishing glass. The specific gravity of these minerals is 3.9; their hardness is only a little below that of the diamond. Artificial aluminium oxide—corundum—may be obtained by reducing metallic oxides with aluminium—following Goldschmidt's method; in making chromium the slag will contain little crystals of the ruby. The crystallized or strongly ignited aluminium oxide is almost insoluble in acids; to decompose it, it is fused with caustic alkalies or with primary potassium sulphate, $HKSO_4$.

Aluminium Hydroxides.—The *normal hydroxide*, $Al(OH)_3$, occurs in nature as hydrargillite. The hydroxide, $Al_2O_2(OH)_2$, is diaspore. Bauxite is a mixture of the hydroxide, $Al_2O(OH)_4$, with ferric oxide. It occurs in large deposits in France, in the Caucasus, etc. The normal hydroxide is artificially obtained as a white voluminous precipitate, by adding ammonium hydroxide or an alkaline carbonate (in the latter case carbon dioxide escapes, p. 352) to a soluble aluminium salt. It dissolves, when freshly precipitated, in acids and in potassium and sodium hydroxides. By long standing under water, or after drying, it is, without any alteration in composition, difficultly soluble in acids. When carefully heated, the normal hydroxide first passes into the hydrate, $AlO.OH$.

The freshly precipitated hydroxide dissolves readily in a solution of aluminium chloride or acetate. On dialyzing (p. 237) this solution the aluminium salt or crystalloid diffuses, and in the dialyzer remains the pure aqueous solution of the hydroxide. This has a faint alkaline reaction and is coagulated by slight quantities of acids, alkalies and many salts; the soluble hydrate passes into the insoluble gelatinous modification.

Gelatinous aluminium hydroxide possesses the property of precipitating many dyestuffs from their solutions, forming colored insoluble compounds (lakes) with them. On this is based the application of aluminium hydroxide as a mordant in dyeing. The acetate is generally used for this purpose. Goods saturated with this salt are heated with steam, which causes the decomposition of the weak acetate; acetic acid is driven off, while the separated aluminium hydroxide adheres to the fiber of the material. If the latter now be introduced into the solution of coloring matter the color will be fixed by the aluminium hydroxide upon the fiber. At present, sodium aluminate is employed instead of the acetate.

Aluminium hydroxide has a feeble acid character, and can form salt-like compounds with strong bases. On carefully evaporating its solution in sodium or potassium hydroxide, or upon addition of alcohol, white amorphous compounds of $KAlO_2$, $NaAlO_2$ and $Al(ONa)_3$ are obtained. The potassium compound can be obtained in crystalline form. These derivatives, known as *aluminates*, are not very stable, and are even decomposed by carbon dioxide, with elimination of aluminium hydroxide:

$$2NaAlO_2 + CO_2 + 3H_2O = 2Al(OH)_3 + Na_2CO_3.$$

The aluminium hydroxide obtained in this manner, in distinction from that precipitated from acid aluminium solutions by the alkalies, is not gelatinous, and is more difficultly soluble in acids, especially acetic. It comprises the ordinary alumina of commerce.

On adding calcium chloride, strontium chloride, or barium chloride to the solution of potassium or sodium aluminate, white insoluble aluminates are precipitated:

$$2NaAlO_2 + CaCl_2 = Ca(AlO_2)_2 + 2NaCl.$$

Similar aluminates frequently occur as crystallized minerals, in nature. Thus the spinels consist chiefly of magnesium aluminate, $\begin{matrix}AlO.O\\AlO.O\end{matrix}>Mg$;

chrysoberyl is beryllium aluminate, $\begin{matrix}\mathrm{AlO.O}\\\mathrm{AlO.O}\end{matrix}\!>\!\mathrm{Be}$; gahnite is zinc aluminate, $\begin{matrix}\mathrm{AlO.O}\\\mathrm{AlO.O}\end{matrix}\!>\!\mathrm{Zn}$.

Nearly all these minerals, commonly called spinels, crystallize in regular octahedra, like the corresponding chromium compounds (see these); the exceptions are chrysoberyl, crystallizing in the rhombic system, and hausmannite, $Mn_3O_4 = \begin{matrix}\mathrm{MnO.O}\\\mathrm{MnO.O}\end{matrix}\!>\!\mathrm{Mn}$, in the quadratic system.

Technically, alumina is obtained from cryolite, bauxite and other minerals containing aluminium. The pulverized bauxite is heated with dry sodium carbonate in furnaces, and the resulting sodium aluminate extracted with water. From the clear solution carbon dioxide precipitates the hydroxide, while sodium carbonate remains dissolved, and is afterward recovered. The dried aluminium hydroxide occurs as a white powder in trade.

K. J. Baeyer treats the finely ground bauxite with caustic soda and stirs into this solution freshly precipitated, crystalline alumina (as obtained on conducting carbon dioxide into a cold aluminate solution). All of the alumina separates after some hours, and the alkaline liquid is again run through the same course. The method is based on the decomposition of the aluminates by water; the alumina which is mixed in with it acts like a crystal of Glauber salt upon supersaturated solutions (p. 288).

The gelatinous, readily soluble (colloidal) aluminium hydroxide (see above) precipitated from acid solutions by alkalies, has lately been prepared upon a large scale, according to the method of Löwig, by treating the sodium aluminate solution with milk of lime; calcium aluminate precipitates, while sodium hydroxide remains in solution:

$$2NaAlO_2 + Ca(OH)_2 = Ca(AlO_2)_2 + 2NaOH.$$

The calcium aluminate is dissolved in hydrochloric acid:

$$Ca(AlO_2)_2 + 8HCl = 2AlCl_3 + CaCl_2 + 4H_2O,$$

and to the solution now containing the alumina as chloride the corresponding amount of calcium aluminate added, and aluminium hydroxide is precipitated:

$$2AlCl_3 + 3Ca(AlO_2)_2 + 12H_2O = 8Al(OH)_3 + 3CaCl_2.$$

According to this procedure, the sodium hydroxide formed in the first reaction is obtained together with the alumina.

On conducting carbon dioxide into a solution of alkaline carbonates, and adding a solution of an alkaline aluminate at the same time, white *aluminium-alkali carbonates* are precipitated:

$$Al_2O_3.K_2O + 2KHCO_3 = Al_2O_3.K_2O.2CO_2 + 2KOH.$$

The caustic alkali that is formed in this way is converted again into bicarbonate by carbon dioxide. In a dry state the precipitates are white, chalk-line masses which at 90° contain five molecules of water:

$$Al_2O_3.K_2O.2CO_2 + 5H_2O.$$

Their constitution may be expressed by the formula:

$$K{-}O{-}CO{-}O{-}Al = O.$$

They dissolve readily in dilute acids, even acetic, with evolution of carbon dioxide, and are suitable for the preparation of pure alumina mordants and antiseptic solutions (Löwig).

The basic character of aluminium hydroxide exceeds the acid; but it is so feeble that it is not capable of forming salts with weak acids, as carbon dioxide, sulphurous acid, and hydrogen sulphide. When sodium carbonate is added to solutions of aluminium salts, aluminium hydroxide is precipitated, while carbon dioxide is set free:

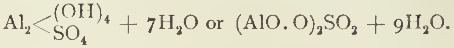
$$2AlCl_3 + 3Na_2CO_3 + 3H_2O = 2Al(OH)_3 + 6NaCl + 3CO_2.$$

The alkaline sulphides behave similarly:

$$2AlCl_3 + 3(NH_4)_2S + 6H_2O = 2Al(OH)_3 + 6NH_4Cl + 3H_2S.$$

That the hydrate is a feeble acid is shown in the decomposition of the alkali salts by carbon dioxide.

Aluminium Sulphate, $Al_2(SO_4)_3$, crystallizes from aqueous solution with eighteen molecules of water in thin leaflets with pearly luster. These dissolve readily in water; when heated, they melt and lose all their water of crystallization. The sulphate is obtained by dissolving the hydroxide in sulphuric acid, or by the decomposition of pure aluminium silicate (clay) with the same acid; the residual silicic acid is removed by filtration, and the solution of the sulphate evaporated. When a quantity of ammonium hydroxide, insufficient for complete precipitation, is added to the sulphate, *basic* sulphates separate out. Salts similar to the latter are also found in nature; thus, aluminite, used to prepare alum, has the composition:



$$Al_2 < \begin{matrix} (OH)_4 \\ SO_4 \end{matrix} + 7H_2O \text{ or } (AlO.O)_2SO_2 + 9H_2O.$$

Aluminium sulphate can combine with the alkaline sulphates and affords double salts, termed *alums, e. g.*, potassium alum:

$$Al_2(SO_4)_3.K_2SO_4 + 24H_2O \text{ or } KAl(SO_4)_2 + 12H_2O.$$

Their constitution is expressed by the following formula:

$$SO_4 = \overset{III}{Al} - SO_4 - K + 12H_2O.$$

In this compound the potassium may be replaced by sodium, ammonium, rubidium, cæsium, and also by thallium hydroxylamine, and some organic bases. Iron, chromium and also vanadium, titanium and manganese afford like derivatives:

$$Fe_2(SO_4)_3.K_2SO_4 + 24H_2O$$

Potassium iron alum.

$$Cr_2(SO_4)_3.(NH_4)_2(SO)_4 + 24H_2O.$$

Ammonium chromium alum.

All these alums crystallize in regular octahedra or cubes, and can form isomorphous mixtures.

The most important of them is *potassium aluminium sulphate* or *ordinary alum*, $KAl(SO_4)_2 + 12H_2O$. It crystallizes from water in large, transparent octahedra, soluble in 8 parts of water of ordinary temperature, or in ⅓ part of boiling water. The solution has an acid reaction and a sweetish, astringent taste. When placed over sulphuric acid, alum loses three-fourths of its water. When heated it melts in its water of crystallization, loses all the latter, and becomes a white, voluminous mass—*burnt alum*. Upon adding a little sodium or potassium carbonate to a hot alum solution, the hydroxide first produced dissolves, and when the liquid cools, the alum crystallizes out in cubes, as *cubical alum*. The addition of more sodium carbonate causes the precipitation of the basic salt—$KAl(SO_4)_2.Al(OH)_3$. Alunite, found in large quantities near Rome and in Hungary, has a similar composition, $K(AlO)_3(SO_4)_2 + 3H_2O$.

Commercial alum is obtained according to various methods: (1) From alunite, by heating and extracting with hot water. In this way alum dissolves while the hydroxide remains; from such solutions the former crystallizes in combinations of the octahedron with cube faces—Roman alum. (2) The most common source of alum was formerly *alum shale*, a clay containing pyrite and peat. This is roasted and after moistening with water is exposed for a long time to the action of the air. By this means pyrite, FeS_2, is converted into ferrous sulphate, $FeSO_4$, and free sulphuric acid, which, acting upon the clay, forms aluminium sulphate. The mass is extracted with water, potassium sulphate added, and the whole permitted to crystallize. (3) At present clay is treated directly with sulphuric acid, and to the solution of aluminium sulphate potassium or ammonium sulphate is added. (4) Bauxite and cryolite are admirable material for the preparation of alum. The working of cryolite for alumina and soda is described on p. 292, and that of bauxite, p. 351).

Ammonium Alum, $NH_4Al(SO_4)_2 + 12H_2O$, crystallizes, like potassium alum, in large crystals, and at present, owing to its cheapness, is applied almost exclusively for technical purposes. *Sodium alum* is much more soluble, and crystallizes with difficulty. As the alum employed in dyeing must contain no iron, we understand why this salt is not applicable. At present the alum is being more and more supplanted by aluminium sulphate and sodium aluminate in all practical operations, because these chemicals can be procured perfectly free from iron.

Aluminium Phosphate, $AlPO_4 + 4H_2O$, is thrown out of aluminium salt solutions by sodium phosphate, as a white gelatinous precipitate; this is readily soluble in acids, acetic excepted. Turquoise is a basic phosphate of aluminium colored blue by a copper compound.

Aluminium Silicates.—The most important of the aluminium double silicates, so widely distributed in nature, are: *leucite*, $KAl(SiO_3)_2$, *albite* or soda feldspar, $NaAlSi_3O_8$, ordinary feldspar—*orthoclase*, $KAlSi_3O_8$, and the various micas, which, with quartz, compose granite. When these disintegrate under the influence of water and the carbon dioxide of the air, alkaline silicates are dissolved and carried away by water, while the insoluble aluminium silicate, *clay*, remains. Perfectly pure clay is white, and is called *kaolin*, or porcelain clay; its composition mostly corresponds to the formula, $Al_4(SiO_4)_3 + 2H_2O$ or $Al_2Si_2O_7 + 2H_2O$. When clay is mixed with water a tough, kneadable mass is obtained. By drying and burning, it becomes compact and hard, and is the more fire-proof, the purer the clay. On this depends the use of clay for the manufacture of earthenware, from the red brick to porcelain.

To produce *porcelain* a very fine mixture of kaolin, feldspar and quartz is employed. On strong ignition, the feldspar fuses, fills the pores of the clay and thus furnishes a fused transparent mass—porcelain. When it is not so strongly ignited, it remains porous—faience—serving for finer clay vessels. To render these impervious to water, they are covered with glazing. This consists of various readily fusible silicates. Rough earthenware vessels are constructed from impure clay, and they are usually glazed by throwing salt into the ovens at the time of burning. The salt vaporizes and forms an easily fusible silicate on the surface of the clay, hydrochloric acid being liberated.

Ultramarine.—The rare mineral *Lapis lazuli*, which was formerly employed as a very valuable blue color under the name of *Ultramarine*, is a compound of aluminium sodium silicate with sodium polysulphides. At present ultramarine is prepared artificially, in large quantities, by heating a mixture of clay, dry soda (or sodium sulphate), sulphur and charcoal, away from air. *Green* ultramarine is the product. This is then washed with water, dried, mixed with powdered sulphur and gently heated with air contact until the desired blue color has appeared—*blue* ultramarine. The chemical constitution of this blue coloring material has not yet been explained. On pouring hydrochloric acid over the blue product, the color disappears with liberation of sulphur and hydrogen sulphide—this would point to the existence of a polysulphide. Violet and red ultramarines are prepared at present by conducting dry hydrogen chloride gas and air over common ultramarine at 100–150°.

RARE EARTH METALS.

In some very rare minerals, like cerite, gadolinite, euxenite, orthite, samarskite, thorite, and monazite, occurring principally in Sweden, Norway, Greenland, and the United States, is found a series of metals which, in their entire deportment, closely resemble aluminium (p. 345). These are scandium, yttrium, cerium, lanthanum, neodymium, praseodymium, samarium, ytterbium, and the more recent erbium, terbium, gadolinium, decipium, thulium, holmium and dysprosium. These generally form difficultly soluble oxalates, and are, therefore, precipitated from solution by oxalic acid. The anhydrous sulphates are quickly and easily soluble in cold water; in warm water they are slowly and difficultly soluble. They form double salts with the alkali sulphates; the potassium double salts are constituted according to the formula $Me_2(SO_4)_3.3K_2SO_4$. Their solubility in water differs; some of them are insoluble in saturated solutions of potassium sulphate. The formates are partly sparingly soluble and in part very soluble. The hydrous nitrates and chlorides are very soluble in water and in alcohol. The nitrates of these metals are decomposed at different temperatures; this property affords an excellent means for their isolation and separation. Fractional precipitation with ammonia is also used for this purpose. The salts and solutions of the individual metals are in part colorless and partly colored. Most of the latter show absorption spectra. The position of the absorption lines in the spectrum—their wave-length—is characteristic for that particular element and is a sure and excellent means for its recognition. The oxides of many of these metals when heated in the Bunsen flame diffuse great quantities of light. The glowing oxides of some of the elements whose salt solutions show absorption spectra give a discontinuous spectrum with bright bands whose positions correspond exactly to the absorption lines.

Scandium, yttrium, lanthanum, cerium, samarium, and ytterbium have been most accurately investigated. Their atomic weights are very approximately correct. The most interesting of the group is scandium, atomic weight 44.1. It fills out the gap between calcium and titanium. It coincides in all its properties with those deduced theoretically from the periodic system by Mendelejeff for the element *ekaboron* (compare Gallium).

Scandium, Sc = 44.1, discovered by Nilson in 1879, is contained in euxenite and gadolinite; it has not yet been obtained in a free condition. Its *oxide*, Sc_2O_3, is obtained by igniting the hydroxide or nitrate, and is a white, infusible powder (like magnesia and oxide of beryllium). Its specific gravity equals 3.86. The *hydroxide*, $Sc(OH)_3$, is precipitated as a gelatinous mass from its salts by the alkalies, and is insoluble in an excess of the latter. The *nitrate* crystallizes in little prisms, and is easily decomposed by heat. The *potassium double sulphate*, $Sc_2(SO_4)_3 . 3K_2SO_4$, is soluble in warm water, but not in a solution of potassium sulphate. The chloride affords a characteristic spark spectrum.

Yttrium—Y = 89, discovered by Mosander in 1843 in the yttria of gadolinite, has been obtained by electrolyzing the anhydrous fused chloride. It is a gray powder which decomposes water in the cold. Cleve and Höglund first obtained many of its compounds in a pure state. It occurs principally in the gadolinite from ytterby (about 35 per cent. Y_2O_3). Its oxide is a white, infusible, strong base, which is capable of expelling ammonia from its salts. Its specific gravity is 5.04. Its *potassium double sulphate*, $Y_2(SO_4)_3.3K_2SO_4$, is soluble in a potassium sulphate solution, and in this manner it can be readily separated from cerium, lanthanum, didymium and samarium. Its *nitrate*, $Y(NO_3)_3 + 6H_2O$, forms large, deliquescent crystals. The *chloride*, $YCl_3 + 6H_2O$, forms large prisms, and gives a brilliant spark spectrum rich in lines.

Lanthanum, La = 138 (from λανθάνειν, to be hidden), was discovered in cerite by Mosander (1839). It can be obtained by the electrolysis of its fused chloride. It resembles iron in color and in luster. It oxidizes in the air and in a flame burns with a bright light. Specific gravity = 6.16. The oxide La_2O_3 is brilliant white; it combines directly with water to the *hydrate* $La(OH)_3$, which reacts alkaline and absorbs carbon dioxide from the air. It is a powerful base which expels ammonia from ammonium salts in the cold. The anhydrous *sulphate*, $La_2(SO_4)_3$, dissolves readily in water of 4°. When its saturated solution is heated to 40° most of it separates as the hydrous salt. The following sulphates are known: $La_2(SO_4)_3 + 6H_2O$ and $La_2(SO_4)_3 + 9H_2O$. The potassium double salt is sparingly soluble in water and insoluble in a saturated potassium sulphate solution, $La_2(SO_4)_3 . 3K_2SO_4$. The *nitrate*, $La(NO_3)_3 . 6H_2O$, consists of large prismatic crystals, which lose water on heating. The salt melts when more strongly heated, and on cooling becomes like dust. It decomposes at high temperatures. The anhydrous chloride, $LaCl_3$, is a crystalline mass, which deliquesces in moist air, forming crystals of the hydrous chloride, $2LaCl_3 . 15H_2O$. The *chloride* shows a very bright spark spectrum with numerous lines. Pure lanthanum oxide exposed in a vacuum to kathode rays shines with a powerful light and before the spectroscope shows a brilliant band spectrum. The lanthanum salts are colorless; they do not have an absorption spectrum.

Cerium, Ce = 140, discovered simultaneously in 1803 by Klaproth and Berzelius and named, as was also the mineral, from the newly discovered planet Ceres, occurs in cerite (60 per cent.), and is also obtained by the electrolysis of the chloride. It is very similar to lanthanum, but at ordinary temperatures is more stable in the air than the latter; it burns much more readily, so that broken-off particles of it inflame of their own accord. The specific gravity of the fused metal is 6.72. Besides the salts of the *sesquioxide*, Ce_2O_3, it forms some from the *dioxide*, CeO_2. The former in which cerium is trivalent are colorless, while the latter—the ceric—are colored yellow or brown; red ceric hydroxide, $Ce(OH)_4$, is precipitated from the former, on the addition of hypochlorites. A little aqueous hydrofluoric acid will convert the ceric hydroxide into *cerium tetrafluoride*, $CeFl_4 + H_2O$. The *tetrachloride*, $CeCl_4$, is also known in double salts. These compounds indicate that cerium is quadrivalent and that it probably belongs to the fourth group of the periodic system (p. 246).

Didymium, Di = 142, was found in cerite by Mosander, and was regarded as an element until 1885. Auer von Welsbach then succeeded in resolving it into two new elements, which he called **Neodymium** = Nd (144?) and **Praseodymium** = Pr (140?). The oxide of the old didymium (from διδύμοι, twins, a constant associate of cerium and lanthanum) has a bright gray color after strong ignition, that of neodymium a bluish color and that of praseodymium a greenish-white color. While the salts of old didymium had an amethyst-red color, those of neodymium are a rose-violet and those of praseodymium are an intense leek-green. The salts and solutions of the old didymium showed a magnificent absorption spectrum and its components share this with it. The same is true of the spark spectra. The most important derivatives of praseodymium were recently prepared and studied by von Schele. It has two oxides: PrO_2 and Pr_2O_3. Its salts follow the type PrX_3; the praseodymium in them is pronouncedly trivalent (Z. f. anorg. Ch. (1898) 17, 310; 18, 352).

Samarium, Sm = 150, was discovered by M. Delafontaine and almost simultaneously by Lecoq de Boisbaudran in 1878 on studying unknown absorption bands given by the samarskite from North Carolina. It has also been found in cerite, gadolinite and orthite. Marignac (1880) prepared the oxide and some salts in a pure state. P. T. Cleve has made an exhaustive investigation of it. The metal has not yet been prepared. The oxide is pure white and its specific gravity is 8.38. In the Bunsen flame it shows a remarkable light-emission power and a discontinuous spectrum with bright bands. Samarium salts are light yellow in color. They and their solutions exhibit a characteristic absorption spectrum. The *sulphate*, $Sm_2(SO_4)_3 + 8H_2O$, consists of small crystals, dissolving with difficulty in water. Its double salt with potassium sulphate is sparingly soluble in water and almost insoluble in a saturated potassium sulphate solution. The *nitrate*, $Sm(NO_3)_3$, crystallizes, melts easily and is decomposed. The *chloride*, $SmCl_3 + 6H_2O$, forms large tabular crystals; its spark spectrum is very distinct.

Ytterbium, Yb = 173. Marignac (1878) found that its oxide was the chief constituent of erbium oxide which Bahr and Bunsen had regarded as a distinct element. It is obtained by the repeated incomplete decomposition of a mixture of the nitrates of these earths with careful heating. Ytterbium and scandium oxides being the feeblest bases, are first eliminated and can then be separated by means of potassium sulphate. Ytterbium oxide, Yb_2O_3, is a white, infusible powder of specific gravity 9.17. It is readily soluble in acids; its salts are colorless and do not show an absorption spectrum. *Ytterbium sulphate*, $Yb_2(SO_4)_3 + 8H_2O$, forms large prisms, stable in the air. Its double salt with potassium sulphate is readily soluble in water and in a saturated potassium sulphate solution. Ytterbium chloride gives a spark spectrum rich in lines.

Erbium = Er. Mosander (1843) demonstrated that the supposedly simple yttria was in fact a mixture of the three earths—erbia, terbia and ytterbia. The erbia of to-day is the rose-red oxide from the old yttria, which Mosander called terbia, and which Bahr and Bunsen (1866), as well as Cleve and Höglund (1873) prepared in large quantities from gadolinite and regarded it as elementary. However, Marignac in 1878 obtained ytterbium from it and Nilson in 1879 scandium. The investigations continued in that line proved that it could be still further simplified. The old erbia gave an absorption spectrum very rich in lines and the fact that on partly decomposing its nitrate by fusion or by the fractional precipitation of its nitrate solution with dilute ammonia, fractions were obtained in which the absorption bands appeared in different number and strength, induced P. T. Cleve to assume in it the presence of three elements—the real **Erbium** = Er (166), **Thulium** = Tm and **Holmium** = Ho. Then Lecoq de Boisbaudran by similar observations discovered that holmium also contained **Dysprosium** = Dy (δυσπρόσιτος, difficult to reach). Nilson and Krüss regard erbium, thulium, holmium, and dysprosium as capable of further division.

Terbium = Tr. The oxide (terbia) was discovered by Mosander in the old yttria, but called erbia by him at that time. It occurs in small quantities in the gadolinite of Ytterby in Sweden. The names, yttrium, erbium, terbium, and ytterbium, are transpositions of the syllables of the word Ytterby. The samarskite from North Carolina contains great quantities of terbia. The metal has not been prepared. Terbia is a dark orange-red powder. It dissolves in hydrochloric acid with evolution of chlorine. It loses its color when heated in hydrogen, also suffers a slight loss in weight and becomes white. Very probably the orange-colored oxide is a peroxide. The terbium salts are colorless; they have no absorption spectrum. Its formate dissolves with difficulty in water. The double sulphates with potassium and sodium sulphate are sparingly soluble in saturated potassium sulphate and sodium sulphate solutions. The chloride does not yield a spark spectrum. Terbia is probably identical with the oxide of **philippium**, discovered by M. Delafontaine, and the oxide of **mosandrium**, by J. Lawrence Smith. Lecoq de Boisbaudran considers that terbia contains two additional earths, which he designates temporarily $Z\alpha$ and $Z\beta$.

Gadolinium, Gd = 156? Marignac discovered its oxide in the North Carolina samarskite. It is also present in some orthites. It is an almost white powder, very soluble in acids. The salts and salt solutions do not exhibit an absorption spectrum; the chloride does not give a spark spectrum. Exposed to the kathode rays of an induction machine in an almost vacuous tube gadolinia gives out a fiery red color, and in the spectroscope has a spectrum with a bright orange-red line, whose wave length $\lambda = \mu\mu$ 6094.

Decipium, Dp = 171? Its oxide *decipia* (from *decipere*, to deceive) was discovered in the samarskite of North Carolina by Delafontaine. It is colorless; its salts also are colorless and show no absorption spectrum. Its double sulphate with potassium sulphate is insoluble in a saturated potassium sulphate solution. Decipium does not give a spark spectrum.

2. THE GALLIUM GROUP.

The three heavy metals, gallium, indium, and thallium, bear the same relation to aluminium which copper, silver, and gold bear to sodium and zinc cadmium, and mercury to magnesium.

Cu	63.6	Zn	65.4	Ga	70	Ge	72	As	75
Ag	107.93	Cd	112	In	114	Sn	118.5	Sb	120
Au	197.2	Hg	200.3	Tl	204.1	Pb	206.9	Bi	208.5

They constitute the corresponding members of the three great periods, and as a second sub-group attach themselves to aluminium, while cerite metals form the first, more basic sub-group (p. 354). The entire character of the three elements under consideration is influenced by this position in the periodic system, because regular relations appear in all directions, as may be observed, for example, in the specific gravities, melting points, and other physical properties in the free metals:

	Ga	In	Tl
Atomic weight, ...	70	114	204.1
Specific gravity, ...	5.9	7.4	11.8
Melting point, ...	30°	176°	290°

Being members of group III of the periodic system, Ga, In, and Tl yield compounds of the trivalent form, and these are analogous to those of aluminium in many respects.

Thallium, like other elements with high atomic weights (Au, Hg, Pb), exhibits great variations from the group properties (p. 321). It yields, for example, not only derivatives of the form TlX_3, but also those of TlX. If we include thallium as a member of the last great period (Pt, Au, Hg, Tl, Pb, Bi), we will discover that, as in the case of the other metals of this series, a remarkable regularity underlies all its forms of combination—the highest as well as the lowest:

$PtCl_2$	AuCl	HgCl	TlCl	$PbCl_2$	$BiCl_3$
$PtCl_4$	$AuCl_3$	$HgCl_2$	$TlCl_3$	$PbCl_4$	BiX_5.

1. GALLIUM.

Ga = 70.

Gallium was discovered in zinc-blende from Pierrefitte, in 1875, by Lecoq de Boisbaudran, by means of the spectroscope. Since then it has been observed in other blendes, and in the clay iron ore of Yorkshire, as well as in the pig-iron of Middlesborough. It is identical with Linnemann's austrium. As early as the year 1869, Mendelejeff, taking the table of the periodic system devised by him as basis, predicted the existence of a metal (standing between aluminium and indium, with an atomic weight of nearly 69), which he named *Eka-aluminium*. Its properties were necessarily deduced from its position in the periodic system. All the properties of gallium known at that time agreed with those of eka-aluminium, and it seemed very probable that this element, which had been theoretically established, was in reality gallium.

As yet gallium has only been found in very small quantity, and is but imperfectly investigated. It is characterized by a spectrum consisting of two violet lines. Separated by electrolysis from an ammoniacal solution of its sulphate, it is a white, hard metal, of specific gravity 5.9, with a fusing point of +30°. It is only superficially oxidized in the air, not altered by water, and is not volatile up to a red heat. Like aluminium, it is scarcely attacked by nitric acid, but dissolves readily in hydrochloric acid, as well as in caustic potash and ammonia with the evolution of hydrogen.

Gallium and aluminium unite to form alloys; those rich in the former metal are liquid at the ordinary temperature, and decompose water as energetically as metallic sodium.

Gallium Oxide, Ga_2O_3, is obtained by igniting the nitrate. It is a white mass which sublimes when heated in a current of hydrogen. The **hydroxide**, $Ga(OH)_3$, is thrown out of the solutions of its salts by the alkalies as a white flocculent precipitate, readily soluble in an excess of the precipitant, but rather difficultly soluble in ammonium hydroxide.

Gallium Chloride, $GaCl_3$, is produced on heating gallium in a current of chlorine gas or in hydrogen chloride; it forms large colorless crystals which fuse at 75°, sublime at about 60° and boil at 215–220°. Its vapor density above 440° corresponds to the formula $GaCl_3$, at 270° very closely to Ga_2Cl_6. The chloride fumes and deliquesces in the air, like aluminium chloride, and decomposes in the evaporation of its aqueous solution.

Gallium Nitrate, $Ga(NO_3)_3$, and **Gallium Sulphate**, $Ga_2(SO_4)_3$, are crystalline and very deliquescent. The latter forms a double salt with ammonium sulphate—similar to the alums:

$$Ga_2(SO_4)_3.(NH_4)_2SO_4 + 24H_2O.$$

Hydrogen sulphide only precipitates gallium from acetic acid solutions.

Gallium Dichloride, $GaCl_2$, is also known. It results on heating the trichloride with metallic gallium. It consists of colorless crystals, melts at 164° and distils at 535°. Its vapor density at 1000° corresponds to the formula $GaCl_2$.

2. INDIUM.

In = 114.

Owing to its resemblance to zinc, indium was regarded as a bivalent metal, and its compounds were supposed to have the formula InX_2; this fixed its atomic weight at 75.6. The specific heat, however, made the atomic weight one and a half times as large (p. 254). Hence it is trivalent and its derivatives are constituted according to the form InX_3. It belongs to the group of aluminium, and, in its derivatives, manifests some similarity to this metal.

It was discovered, in 1863, by Reich and Richter, by the aid of spectrum analysis. Its spectrum is characterized by a very bright indigo-blue line, hence its name. It only occurs in very minute quantities in some zinc-blendes from Freiberg and the Hartz.

It is a silver-white, soft and tenacious metal, of specific gravity 7.42. It melts at 176° and distils at a white heat. At ordinary temperatures it is not altered in the air;

heated, it burns with a blue flame to indium oxide. It is difficultly soluble in hydrochloric and sulphuric acids, but dissolves readily in nitric acid.

Indium Chloride, $InCl_3$, results from the action of chlorine on metallic indium, or upon a heated mixture of indium oxide and carbon. It sublimes in white, shining leaflets, which deliquesce in the air. Its vapor density at 600–800° corresponds to the formula $InCl_3$, but above 840° it undergoes a gradual decomposition. It does not decompose when its aqueous solution is evaporated.

Indium Oxide, In_2O_3, is a yellow powder resulting from the ignition of the hydroxide.

Indium Hydroxide, $In(OH)_3$, is precipitated as a gelatinous mass, by alkalies, from indium solutions. It is soluble in sodium and potassium hydroxides.

Indium Nitrate, $In(NO_3)_3$, crystallizes with three molecules of water, in white deliquescent needles.

Indium Sulphate, $In_2(SO_4)_3$, remains on evaporating a solution of indium in sulphuric acid as a gelatinous mass, with three molecules of water. It forms an alum with ammonium sulphate.

Indium Sulphide, In_2S_3, is precipitated by hydrogen sulphide as a yellow-colored compound from indium solutions. It combines to sulpho-salts, *e. g.*, $InS.SK$ (from $InO.OH$) with the sulphides of the alkalies.

Indium also forms a dichloride and monochloride.

Indium Dichloride, $InCl_2$, is produced when metallic indium is heated in a current of hydrogen chloride. It is a white crystalline mass, which on exposure to a more intense heat becomes a yellow liquid and sublimes. Its vapor density at 1000–1400° corresponds to the formula $InCl_2$. Water decomposes it at once into indium trichloride and metallic indium: $3InCl_2 = 2InCl_3 + In$.

Indium Monochloride, $InCl$, like gallium dichloride (p. 358), results when the dichloride is heated with metallic indium. It is a crystalline, reddish-yellow mass, which has a reddish-black color when fused. Its vapor density at 1100–1400° corresponds to the formula $InCl$. Water decomposes it into the trichloride and metallic indium: $3InCl = InCl_3 + 2In$.

3. THALLIUM.

$Tl = 204.1.$

Thallium is rather widely distributed in nature, but in very small quantity. The very rare mineral *crookesite* contains 17 per cent. of the metal, together with copper, selenium and silver. It is often found with potassium in sylvite and carnallite, in mineral springs, and in some varieties of pyrite and zinc-blendes. When these pyrites are roasted for the production of sulphuric acid, according to the chamber process, the thallium deposits as soot in the chimney and in the chamber sludge, and was discovered in the latter, almost simultaneously, by Crookes (1861) and Lamy (1862), by means of the spectroscope.

To get the thallium, the chimney-dust is boiled with water or sulphuric acid, and thallous chloride precipitated from the solution by hydrochloric acid. The chloride is then converted into sulphate, and the metal separated from the latter by means of zinc or the electric current.

Thallium is a white metal, as soft as sodium, and has the specific gravity 11.8. It melts at 290°, and distils at a white heat. It oxidizes very rapidly in moist air. It does not decompose water at ordinary temperatures. It is, therefore, best preserved under water in a closed vessel. By air access it gradually dissolves in the water, forming thallous hydroxide and carbonate. Heated in the air it burns with a beautiful green flame whose spectrum shows a very intense green line, hence the name thallium, from ϑαλλός, green. Thallium dissolves readily in sulphuric and nitric acids, but is only slightly attacked by hydrochloric acid, owing to the insolubility of thallous chloride.

Thallium forms two series of compounds: **thallous,** $\overset{I}{Tl}X$, and **thallic,** $\overset{III}{Tl}X_3$. The first are very similar to the compounds of the alkalies (and also to those of silver). The solubility of the hydroxide and carbonate in water shows this; their solutions have an alkaline reaction. Again, many thallous salts are isomorphous with those of potassium, and form similar double salts (see Alums, p. 352). In the insolubility of its sulphur and halogen compounds, univalent thallium approaches silver and lead.

In its compounds of the form TlX_3 thallium is trivalent, like aluminium, but otherwise shows scarcely any similarity to the latter.

Thallium compounds are poisonous. They are used in making thallium glass, which refracts more strongly than lead glass.

THALLOUS COMPOUNDS.

Thallous Oxide, Tl_2O, is formed by the oxidation of thallium in the air, or by heating the hydroxide to 100°. It is a black powder which dissolves in water with formation of the hydroxide.

Thallous Hydroxide, $Tl(OH)$, may be prepared by decomposing thallous sulphate with an equivalent amount of barium hydroxide, and crystallizes with one molecule of water in yellowish prisms. It dissolves readily in water and alcohol, yielding strong alkaline solutions.

Thallous Chloride, $TlCl$, forms on heating, the metal in hydrochloric acid gas and is thrown down from solutions of thallous salts by hydrochloric acid as a white, curdy precipitate, which is difficultly soluble in water. It separates in small crystals from the hot solution. It fuses at 427°, and boils at about 715°. Like potassium chloride, it forms an insoluble double salt with platinic chloride, $PtCl_4.2TlCl$. *Thallous bromide* forms a white, and *thallous iodide* a yellow precipitate. The latter is not soluble in potassium iodide.

Thallous Sulphate, Tl_2SO_4, crystallizes in rhombic prisms, isomorphous with potassium sulphate. It dissolves in 20 parts of water at ordinary temperatures. It affords double salts with the sulphates of the metals of the magnesium group, of ferrous oxide, of cupric oxide, etc. (p. 315), *e. g.*, $MgSO_4.Tl_2SO_4 + 6H_2O$; these are perfectly similar and analogous to the corresponding double salts of potassium and ammonium. It forms thallium alum with the sulphates of the sesquioxides of the iron group, *e. g.*, $TlAl(SO_4)_2 + 12H_2O$; these are similar to potassium alum, $KAl(SO_4)_2 + 12H_2O$.

Thallous Carbonate, Tl_2CO_3, is obtained from the oxide by the absorption of carbon dioxide; it crystallizes in needles, which dissolve at ordinary temperatures in 20 parts of water. The solution has an alkaline reaction.

Thallous Sulphide, Tl_2S, is precipitated from thallous salts by hydrogen sulphide as a black compound, insoluble in water.

THALLIC COMPOUNDS.

Thallic Chloride, $TlCl_3$, is produced by the action of chlorine upon thallium or thallous chloride in water, and is very soluble in the latter. It decomposes at 100° into thallous chloride and chlorine. The alkalies precipitate from its solutions **thallic hydroxide,** $TlO.OH$, a brown powder, which, at 100°, passes into **thallic oxide,** Tl_2O_3. Further heating decomposes the latter into thallous oxide and oxygen.

The oxide and hydroxide are soluble in hydrochloric, nitric, and sulphuric acids, forming $TlCl_3$, $Tl(NO_3)_3$, $Tl_2(SO_4)_3$.

On conducting chlorine through a solution of thallic hydroxide in potassium hydroxide, it assumes an intense violet color, due probably to the formation of the potassium salt of *thallic acid*, the composition of which is yet unknown.

METALS OF THE FOURTH GROUP.

The elements of group IV in the periodic system (p. 246),

	Ti = 48.1	Zr = 90.6	Ce = 140	Th = 282
C = 12.00	Si = 28.4			
		Ge = 72	Sn = 118.5	Pb = 206.9,

show the same analogies that were observed with the members of group III (p. 345). Their character is, however, non-metallic; their derivatives are chiefly of the types MeX_4 and MeO_2, of which the latter are acid (p. 258).

The first two elements, carbon and silicon, with low atomic weights, belong to the two small periods and are true metalloids. Their oxides and hydroxides are acid in nature. The first more basic sub-group comprises titanium, zirconium, cerium, and thorium. They constitute the fourth members of the large periods. Their compounds are almost exclusively of the type MeO_2, are very similar to the silicon derivatives, and are usually discussed (with the exception of cerium) with the metalloids after silicon (pp. 238, 355). The other sub-group consists of more electro-negative heavy metals: germanium, tin, and lead. These constitute the transition from the elements in group III, corresponding to them, to those of group V:

Ga 70	Ge 72	As 75
In 114	Sn 118.5	Sb 120
Tl 204.1	Pb 206.9	Bi 208.5.

Their intermediate position accounts for their metalloidal character. In this group, as in all other groups, it is noticed that as the atomic weight rises (from germanium to lead) there is a successive rise in metallo-basic character. All three members form dioxides,

$$GeO_2 \qquad SnO_2 \qquad PbO_2,$$

which may be viewed as anhydrides of the acids

$$H_2GeO_3 \qquad H_2SnO_3 \qquad H_2PbO_3.$$

These are perfectly analogous to silicic acid, but their stability and acidity diminish as the atomic weights of their basal elements increase.

Lead dioxide, PbO_2, combines with bases (especially the alkalies), forming salts of plumbic acid, *e. g.*, potassium plumbate, K_2PbO_3. These are not very stable; water decomposes them into their components. Lead dioxide unites with difficulty with acids to yield salts. When digested with sulphuric acid it liberates an atom of oxygen, and forms salts of lead monoxide, PbO. It yields chlorine with hydrochloric acid, but in the cold the unstable tetrachloride, $PbCl_4$, can be obtained. In this respect lead dioxide resembles the peroxides, *e. g.*, manganese peroxide, MnO_2, and is commonly known as lead peroxide. However, the salts, Me_2PbO_3, $PbCl_4$, and the organo-metallic compounds, such as $Pb(CH_3)_4$, argue in favor of quadrivalent lead, and make it perfectly analogous to tin (p. 258).

The elements of this group yield monoxide derivatives,

GeO SnO PbO.

These are commonly known as *ous* compounds. They are basic and only form salts with acids. The basicity and stability of their derivatives increase as the atomic weights rise. The german*ous* and stann*ous* compounds are readily oxidized to derivatives of the dioxide type, while lead monoxide, PbO, is a strong base, and forms very stable salts.

1. GERMANIUM.

$Ge = 72$.

This element was discovered in 1886 by Cl. Winkler, of Freiberg. As early as 1871 Mendelejeff, with the periodic system as his basis, predicted the existence of an element with an atomic weight of about 73, which corresponded to the then existing gap between silicon and tin; he called it *ekasilicon* (the first analogue of silicon). The perfect agreement of the essential properties of germanium with those of the theoretical ekasilicon constitutes a brilliant confirmation of the law of periodicity (p. 357).

Winkler discovered germanium in the very rare mineral, argyrodite. The latter is a double sulphide of germanium and silver, $Ge_2S . 3Ag_2S$. Penfield claims the formula $GeS_2 . 4Ag_2S$ for argyrodite as well as for confieldite. The first is monoclinic and the second isometric. It is also present in minute quantities in euxenite (together with titanium and zirconium) (Krüss), in samarskite and frankëite. It may be separated from these minerals by fusing them with sulphur and soda. Sodium sulphogermanate is then produced, and it is soluble in water (p. 363).

To obtain free germanium, its dioxide is heated in a current of hydrogen or reduced with carbon. The product is a dark-gray powder, which melts at 900°, and upon solidifying readily crystallizes into beautiful, grayish-white, metallic octahedra. Its specific gravity at 20° equals 5.469. Its specific heat was found equal to 0.0737 at 100°, and at 440°, 0.0757. Therefore, its atomic heat at 100° is 5.33 and at 440°, 5.45. It increases very slightly (like those of aluminium and silicon) with rise of temperature and is a little less than the mean atomic heat (p. 254).

Germanium is very stable in the air. When ignited it burns with the production of white vapors of germanium dioxide, GeO_2. The metal (like silicon) is insoluble in hydrochloric acid. Nitric acid converts it (like tin) into the hydrate of the dioxide. It is soluble in alkalies upon fusion. When heated in the non-luminous gas-flame, germanium and its compounds do not impart a color to the same. Its spectrum can only be produced by the action of the induction spark.

Germanium, like tin, forms derivatives of the oxides GeO and GeO_2; the first are called german*ous* compounds, the latter german*ic*, or derivatives of germanic acid.

GERMANOUS COMPOUNDS.

These are not very stable, and are readily oxidized to the higher form.

Germanous Oxide, GeO, is formed when the hydroxide is ignited in a current of carbon dioxide. It is a grayish-black powder. **Germanous Hydroxide**, $Ge(OH)_2$, is precipitated as a yellow-colored compound upon the addition of caustic alkali to the solution of the dichloride. It is soluble in hydrochloric acid.

Germanous Chloride, $GeCl_2$, has not been obtained pure. It is formed when hydrochloric acid gas acts upon heated germanous sulphide.

Germanous Sulphide, GeS, is a reddish-brown precipitate produced by the action of hydrogen sulphide upon the solution of the dichloride. It may be obtained in grayish-black crystals by heating germanium sulphide in hydrogen gas. It is soluble in hot hydrochloric acid, forming the corresponding chloride.

GERMANIC COMPOUNDS.

Germanium Tetrachloride, $GeCl_4$, is formed by the direct union of germanium with an excess of chlorine. The metal, when gently heated, burns in an atmosphere of chlorine, with a bluish color. When in powder form it inflames at the ordinary temperature. The tetrachloride is also produced if the sulphide, GeS_2, be heated together with mercuric chloride. It is a colorless, mobile liquid, of specific gravity 1.887 at 18°. It boils at 86°. It fumes strongly in moist air, and is decomposed by water into hydrochloric acid and germanic hydroxide, $Ge(OH)_4$. It is not decomposed by concentrated sulphuric acid. Its vapor density, from 300–740°, corresponds to the molecular formula, $GeCl_4$.

Germanium Chloroform, $GeHCl_3$, corresponding to ordinary chloroform, $CHCl_3$ (see p. 159), is produced when metallic germanium is heated in a current of hydrochloric acid gas. It is a mobile liquid, boiling at about 72°. Its vapor density approximates the molecular formula $GeHCl_3$. It becomes cloudy on exposure to the air, and colorless, oily drops of **Germanium Oxychloride**, $GeOCl_2$ (?), separate.

Germanium Bromide, $GeBr_4$, is a strongly fuming liquid, which solidifies at 0° to a crystalline mass.

Germanium Iodide, GeI_4, results upon heating germanium chloride with potassium iodide, or more readily by conducting iodine vapor over heated and finely divided metal. It is an orange-colored solid, melting at 144°, and boiling at 400°.

Germanium Dioxide, GeO_2, germanic anhydride, is formed upon roasting the metal or the disulphide, or by treating the latter with nitric acid. It is a stable, white powder, of specific gravity 4.70 at 18°. It is slightly soluble in water (1 part in 95 parts at 100°) and imparts to the latter an acid reaction. **Germanic Hydroxide**, $Ge(OH)_4$, or $GeO(OH)_2$, **Germanic Acid**, is produced by directly transposing the chloride with water. It has not been obtained perfectly pure, as it loses more or less water. Like silicic acid, it is wholly acid in its character, and only forms salts with bases. It is soluble in the hydroxides and carbonates of the alkalies, especially on fusion, while it is almost insoluble in acids.

Germanic Sulphide, GeS_2. Concentrated hydrochloric acid or sulphuric acid will precipitate it from solutions of its sulpho-salts. It is also formed when hydrogen sulphide is conducted through strongly acidulated solutions of the oxide. It is a white, voluminous precipitate, insoluble in acids, but readily soluble in water. If the precipitate is washed with water it dissolves. It is reprecipitated by acids, especially if hydrogen sulphide be conducted through the solution. The sulphide dissolves readily in the fixed alkaline hydroxides and ammonia. It forms *sulpho*-salts with the alkaline sulphides. These are perfectly analogous to the sulpho-stannates. Argyrodite is an example of this class, $Ag_2GeS_3 + 2Ag_2S$ (p. 362).

2. TIN.

$Sn = 118.5.$

Tin (*Stannum*) occurs in nature principally as dioxide (cassiterite, tinstone) on the Malay Peninsula, in the islands of Banca and Bilitong, and in England (Cornwall), Saxony, India, and in Australia. To prepare the metal the oxide is roasted, lixiviated, and heated in a furnace with charcoal:

$$SnO_2 + 2C = Sn + 2CO.$$

Thus obtained, it usually contains iron, arsenic, and other metals; to purify it the metal is fused at a low temperature, when the pure tin flows away, leaving the other metals. The tin obtained in the East Indian isles is almost chemically pure, while that of England and of Saxony contains traces of arsenic and copper.

Tin is an almost silver-white, strongly lustrous metal, with a specific gravity of 7.3. It possesses a crystalline structure; and when a rod of it is bent it emits a peculiar sound (tin cry), due to the friction of the crystals. Upon etching a smooth surface of tin with hydrochloric acid, its crystalline structure is recognized by the appearance of remarkable striations. At low temperatures perfectly pure compact tin passes gradually into an aggregate of small quadratic crystals. The metal is tolerably soft, and very ductile, and may be rolled out into thin leaves (tin-foil). It becomes brittle at 200°, and may then be powdered. It fuses at 231°, and distils at a white heat (about 1700°); it burns with an intense white light when heated in the air, and forms tin dioxide. It does not oxidize in the air at ordinary temperatures, and withstands the action of many bodies, hence is employed in tinning copper and iron vessels for household use.

The most interesting of the tin alloys, besides bronze and soft solder, is britannia metal. It contains 9 parts of tin and 1 part of antimony, and frequently, also, 2–3 per cent. of zinc and 1 per cent. of copper.

Tin dissolves in hot hydrochloric acid, to stannous chloride, with evolution of hydrogen gas:

$$Sn + 2HCl = SnCl_2 + 2H.$$

Concentrated sulphuric acid, when heated, dissolves tin, with formation of stannous sulphate.

Nitric acid, depending upon the temperature and the concentration of the acid, forms soluble stannous nitrate or solid stannic nitrate, which separates and is converted by the increasing dilution of the acid or by hot water into a basic salt and stannic acid. Different stannic acids result in accordance with the conditions of experiment. Anhydrous nitric acid, HNO_3, does not change tin. It dissolves when boiled with potassium or sodium hydroxides, forming stannates:

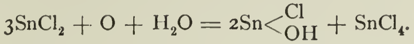
$$Sn + 2KOH + H_2O = K_2SnO_3 + 2H_2.$$

There are two series of compounds: the stannous, and stannic or compounds of stannic acid. The first readily oxidize to stannic compounds.

STANNOUS COMPOUNDS.

Tin Dichloride or *Stannous chloride*, $SnCl_2$, results when tin dissolves in concentrated hydrochloric acid. When its solution is evaporated it crystallizes with two molecules of water ($SnCl_2 + 2H_2O$), which it loses at 100°. It is used in dyeing, as a mordant, under the name of *tin salt*. The anhydrous chloride, obtained by heating the metal in dry hydrochloric acid gas, fuses at 250° and distils without decomposition at 606°. Its vapor density at 900° agrees with the formula $SnCl_2$, while at lower temperatures the molecules Sn_2Cl_4 also seem to exist.

Stannous chloride dissolves readily in water. Its solution is strongly reducing, and absorbs oxygen from the air with the separation of basic stannous chloride:



$$3SnCl_2 + O + H_2O = 2Sn{<}{Cl \atop OH} + SnCl_4.$$

In the presence of hydrochloric acid, only stannic chloride is produced. Stannous chloride precipitates mercurous chloride or metallic mercury from solutions of mercuric chloride (p. 325). It unites with chlorine to form stannic chloride, and with many chlorides to yield double salts, *e. g.:*

$$SnCl_2 . 2KCl \text{ and } SnCl_2 . 2NH_4Cl.$$

It is decomposed by concentrated hydrochloric acid with evolution of hydrochloric acid gas.

Tin Monoxide or *Stannous oxide*, SnO, is obtained by heating its hydroxide, $Sn(OH)_2$, in an atmosphere of carbon dioxide; it is a blackish-brown powder, which burns when heated in the air, and becomes stannic oxide. Sodium carbonate added to a solution of stannous chloride precipitates white

Stannous Hydroxide, *stanno-hydrate*, $Sn(OH)_2$:

$$SnCl_2 + Na_2CO_3 + H_2O = Sn(OH)_2 + 2NaCl + CO_2.$$

It is insoluble in ammonium hydroxide, but is readily dissolved by potassium hydroxide. Upon slow evaporation of the alkaline solution, dark crystals of stannous oxide, SnO, separate; but, on boiling the solution, the hydrate decomposes into potassium stannate, K_2SnO_3, which remains dissolved, and metallic tin:

$$2K_2SnO_2 + H_2O = K_2SnO_3 + 2KOH + Sn.$$

The hydroxide forms salts by its solution in acids. *Stannous chloride*, $SnCl_2$, and *stannous sulphate*, $SnSO_4$, are formed when tin is warmed with concentrated hydrochloric or sulphuric acid. The sulphate separates in small, granular crystals, when its solution is evaporated.

Tin Monosulphide, *Stannous sulphide,* SnS, is precipitated from stannous solutions by hydrogen sulphide, as a dark-brown amorphous precipitate. Obtained by fusing tin and sulphur together, it is a lead-gray crystalline mass. It dissolves in concentrated hydrochloric acid, with liberation of hydrogen sulphide, and forms stannous chloride. It is insoluble in alkaline monosulphides, but, if sulphur be added and the solution boiled, it will dissolve as a sulpho-stannate (p. 367):

$$SnS + S + K_2S = K_2SnS_3.$$

STANNIC COMPOUNDS.

Tin Tetrachloride, *Stannic chloride,* $SnCl_4$, is produced by the action of chlorine upon heated tin or stannous chloride (see Lorenz, Z. f. anorg. Ch. **10** (1895) 44). It is a colorless liquid (*Spiritus fumans Libavii*), fuming strongly in moist air, of specific gravity 2.27, and boiling at 114°; its vapor density corresponds to the molecular formula, $SnCl_4$. It attracts moisture from the air and is converted into a crystalline mass (butter of tin), $SnCl_4 + 3H_2O$, readily soluble in water. Boiling decomposes the solution into metastannic acid (H_2SnO_3) and hydrochloric acid:

$$SnCl_4 + 3H_2O = H_2SnO_3 + 4HCl.$$

Stannic chloride possesses a salt-like nature, and combines with metallic chlorides to the so-called double salts, *e. g.*, $SnCl_4 . 2KCl$ and $SnCl_4 . 2NH_4Cl$; the latter compound is known as *pink salt* and is used in calico printing. It also yields crystalline double salts with chlorides of the metalloids, *e. g.*, $SnCl_4 . PCl_5$ and $SnCl_4 . 2SCl_4$. It is not attacked by even hot concentrated sulphuric acid.

Tin tetrachloride combines with hydrochloric acid, forming $H_2SnCl_6 + 6H_2O$, analogous to the chlorplatinic acid, $H_2PtCl_6 + 6H_2O$. It is formed when hydrochloric acid gas is conducted into a concentrated solution of tin tetrachloride in water. In the cold it solidifies to a leafy crystalline mass, melting at +9°. These double compounds can also be regarded as salts of hydrochlorstannic acid, *e. g.*, $(NH_4)_2SnCl_6$.

Tin Bromide, $SnBr_4$, forms a white, crystalline mass that melts at 30° and boils at 200°. It unites with hydrogen bromide, forming $H_2SnBr_6 + 8H_2O$, crystallizing in yellow needles and plates.

Tin Iodide, SnI_4, formed upon heating tin and iodine at 50°, consists of orange-red octahedra, fusing at 146° and boiling at 295°. A solution of tin iodide in arsenic tribromide (p. 146) has the specific gravity 3.73 at 15°; it is therefore the heaviest solution specifically of which we have knowledge.

Tin Fluoride, $SnFl_4$, is only known in combination with metallic fluorides (*e. g.*, K_2SnFl_6), which are very similar to and generally isomorphous with the salts of hydrofluosilicic acid (K_2SiFl_6).

Tin Dioxide, *Stannic oxide,* SnO_2, is found in nature as tin-stone or cassiterite, in quadratic crystals or compact, brown masses, of specific gravity 6.8. It is prepared, artificially, by heating tin in the air, and it then forms a white amorphous powder, or long, rhombic leaflets. It may be obtained crystallized, by conducting vapors of the tetrachloride and water through a tube heated to redness. The dioxide fuses in the electric furnace, and is not soluble in acids or alkalies. When fused with sodium and potassium hydroxide it yields stannates soluble in water.

The dioxide forms two hydrates—the stannic acids, H_2SnO_3 and H_4SnO_4—corresponding to the hydrates H_2CO_3, H_2SiO_3 and H_4CO_4 and H_4SiO_4 (p. 226). Each of these two acids is known in two varieties which differ very much from one another in their deportment. This double appearance of similarly constituted stannic acids was the first instance of isomerism (p. 87). Berzelius (1811) observed it, but he did not comprehend its full import until after (1817) the investigations of Davy and Gay Lussac had been made. Tin and nitric acid of specific gravity 1.35 yield stannic nitrate and the β- or *metastannic acid*, of the formula H_2SnO_3 or H_4SnO_4, depending on its method of preparation. It is white, voluminous and insoluble in acids. It only dissolves when freshly made in sodium hydroxide. An excess of soda precipitates sodium metastannate from this solution; it dissolves in pure water.

The acid upon which hydrochloric acid has been poured dissolves in pure water. Sulphuric acid reprecipitates it. α-Stannic acid—also H_2SnO_3 or H_4SnO_4—is precipitated as a voluminous white powder on the addition of alkali to solutions of the tetrachloride or bromide which have not stood too long. It dissolves readily while moist in mineral acids and in sodium hydroxide, even when the latter is in excess. Both acids separate on heating their dilute hydrochloric acid solutions or upon the addition of ammonia water. The presence of tartaric acid prevents the precipitation of the α-acid by ammonia. The α-acid in hydrochloric acid solution gradually passes into the β-acid (Lorenz, Z. f. anorg. Ch. 9 (1895), 368). The reason for this first observed case of isomerism has not been explained.

Most of the salts of stannic oxide with acids, *e. g*, the sulphate, are not very stable, and washing with warm water decomposes them. The phosphate and arsenate are exceptions. They are insoluble in water and in nitric acid, which is of importance in analysis. The metallic salts of the stannic acids are more stable. The most important of these is *α-sodium stannate*, $Na_2SnO_3 + 3H_2O$, which is employed in calico printing under the name of *preparing salts*. It is produced upon a large scale by fusing tin-stone with sodium hydroxide. On evaporating the solution, it crystallizes in large, transparent, hexagonal crystals.

Tin Disulphide, *Stannic sulphide*, SnS_2, is precipitated as an amorphous yellow powder by hydrogen sulphide from acid solutions of stannic salts. If a mixture of tin filings, sulphur, and ammonium chloride be heated it is obtained in the form of a brilliant crystalline mass, consisting of gold-yellow scales. It is then called *mosaic gold*, and is applied in bronzing. Concentrated hydrochloric acid dissolves the precipitated disulphide, forming stannic chloride; nitric acid converts it into metastannic acid. The sulphides and hydrosulphides of the alkalies dissolve tin disulphide, forming sulphostannates (see p. 223). *Sodium sulphostannate*, $Na_2SnS_3 + 2H_2O$, crystallizes in colorless octahedra. Acids decompose the sulphostannates with the separation of tin disulphide and the evolution of hydrogen sulphide. Freshly precipitated tin disulphide dissolves rather readily in aqueous ammonia forming a red liquid which becomes colorless after standing in the air for some time. From this solution acids precipitate a white tin *oxysulphide*, $SnS_2 + SnSO$, soluble in aqueous ammonium carbonate.

3. LEAD.

$Pb = 206.9$

Lead (*Plumbum*) is found in nature principally as *galenite*, PbS. The other more widely distributed lead ores are *cerussite*, $PbCO_3$, *crocoisite* ($PbCrO_4$), *wulfenite* ($PbMoO_4$); also *pyromorphite*, $PbCl_2 + 3Pb_3(PO_4)_2$-

$+H_2O$; *anglesite*, $PbSO_4$, and *bournonite*, $PbS.Sb_2S_3$. The countries of importance in the industry of lead are the United States, Spain, Germany, Great Britain, and New South Wales. Galenite is the chief source of lead; the process of its separation is very simple. The galenite is first roasted in the air and then strongly ignited away from it. In the roasting, a portion of the lead sulphide is oxidized to oxide and sulphate:

$$PbS + 3O = PbO + SO_2$$

and

$$PbS + O_4 = PbSO_4.$$

Upon ignition, these two substances according to Percy react with the lead sulphide according to the following equations:

$$2PbO + PbS = 3Pb + SO_2$$

and

$$PbSO_4 + PbS = 2Pb + 2SO_2.$$

Galenite may also be fused with iron: $PbS + Fe = FeS + Pb$. Iron sulphide, containing lead sulphide, is used in making sulphur dioxide for the lead-chamber process. The resulting work-lead is contaminated with nearly all the metals which occur in ores. They are eliminated by rather complex methods.

Pure metallic lead has a bluish-white color, is very soft, and tolerably ductile. A freshly cut surface has a bright luster, but on exposure to air becomes dull by oxidation. Its specific gravity is 11.37. It melts at about 300°, and distils at a white heat (about 1700°). It burns to lead oxide when heated in the air.

In contact with air and pure water lead oxidizes to lead hydroxide, $Pb(OH)_2$, which is somewhat soluble in water. If, however, the water contain carbonic acid and mineral salts—even in slight quantity, as in natural waters—no lead goes into solution, but it is covered with an insoluble layer of lead carbonate and sulphate. When much carbon dioxide is present the carbonate is somewhat soluble in water. This behavior is very important for practical purposes, as lead pipes are frequently employed in conducting water. Lead also dissolves in ammonia and lime-water in the presence of air.

Sulphuric and hydrochloric acids have little effect on the compact metal, owing to the insolubility of its sulphate and chloride; yet, if the lead be in the form of powder, both acids will dissolve it. It forms lead nitrate with dilute nitric acid. Zinc, tin, and iron precipitate it, as metal, from its solution; a strip of zinc immersed in a dilute solution of lead acetate is covered with an arborescent mass, consisting of shining crystalline leaflets (lead tree).

Alloys.—An alloy of equal parts of lead and of tin fuses at 186°, and is used for soldering (soft solder). An alloy of 4–5 parts of lead and 1 part of antimony is very hard, and answers for the manufacture of type (hard lead or type-metal). Shot are lead containing 0.2–0.35 per cent. of arsenic.

The usual lead compounds are constituted according to the type PbX_2, and are called *plumbic* (p. 357). Many of the lead salts are isomorphous with those of barium; the sulphates of both metals are insoluble in water. In addition to the salts of the type PbX_2 lead also forms that of the type PbX_4, which are, however, very unstable.

Lead Oxide, PbO, is produced when lead is heated in air. It melts at a red heat and after fusion it solidifies to a reddish-yellow mass of rhombic scales (litharge). When lead is carefully roasted, or the hydroxide or nitrate ignited, we obtain a yellow amorphous powder called massicot. Lead oxide has strong basic properties; it absorbs carbon dioxide from the air, and imparts an alkaline reaction to water as it dissolves as hydroxide. Like other strong bases it saponifies fats (lead plaster). It dissolves in hot potassium hydroxide, and on cooling crystallizes from solution in yellow rhombic or red tetragonal forms, depending upon existing conditions [Geuther, Ann. Chem. **219** (1883), 56].

Lead Hydroxide, $Pb(OH)_2$. Alkalies throw it out of lead solutions as a white, voluminous precipitate.

It dissolves slightly in water, and absorbs carbon dioxide with formation of lead carbonate. When heated to 130° it decomposes into lead oxide and water. It is soluble in caustic potash or soda.

If lead or the amorphous oxide be heated to 300–400°, for some time, in the air, it will absorb oxygen and be converted into a bright red powder, called *red lead*, or minium. Its composition corresponds to the formula Pb_3O_4; it is considered a compound of lead monoxide with lead peroxide:

$$Pb_3O_4 = 2PbO + PbO_2.$$

When minium is treated with dilute nitric acid, lead nitrate passes into solution, while a dark-brown amorphous powder, **lead peroxide**, PbO_2, remains.

This oxide is more conveniently obtained by the interaction of lead carbonate and sodium hypochlorite, *e g.*, if a solution of lead acetate be mixed with an excess of sodium carbonate and chlorine be conducted into the pasty mass:

$$PbCO_3 + Na_2CO_3 + Cl_2 = PbO_2 + 2NaCl + 2CO_2.$$

Lead peroxide dissolves in ice-cold concentrated hydrochloric acid to a reddish-yellow liquid containing *lead tetrachloride*, $PbCl_4$.

Oxygen is disengaged when sulphuric acid acts upon it, and lead sulphate ($PbSO_4$) is formed. When dry sulphur dioxide is conducted over it, glowing sets in and lead sulphate results:

$$PbO_2 + SO_2 = PbSO_4.$$

When ignited lead dioxide breaks down into lead monoxide and oxygen.

Lead dioxide, when warmed with potassium hydroxide, dissolves, and on cooling, large crystals of *potassium plumbate*, $K_2PbO_3 + 3H_2O$, separate out; these are perfectly analogous to potassium stannate, $K_2SnO_3 + 3H_2O$. An alkaline lead oxide solution added to a solution of potassium plumbate produces a yellow precipitate ($Pb_3O_4 + H_2O$), which loses water upon gentle warming, and is converted into *red lead*. Therefore, the latter must be considered as the lead salt of a normal plumbic acid, $Pb(OH)_4$, which corresponds to stannic, $Sn(OH)_4$, and silicic, $Si(OH)_4$, acids:

$$Pb_3O_4 = Pb_2PbO_4.$$

The calcium salt,—calcium orthoplumbate, Ca_2PbO_4,—is produced upon igniting lead peroxide with lime or calcium carbonate, or when lead oxide and lime are heated with air access, *i. e.*, the absorption of oxygen. It is a yellowish-red substance, which breaks down when heated in carbon dioxide into lead oxide, calcium carbonate and oxygen:

$$Ca_2PbO_4 + 2CO_2 = PbO + 2CaCO_3 + O_2.$$

The resulting mixture of lead oxide and chalk regenerates calcium plumbate when it is heated in an air current (Kassner's oxygen method).

Lead peroxide and other oxides of lead play an important part in charging accumulators with electricity. In the process of charging the lead oxide at the negative plate is decomposed into lead and oxygen, while at the positive pole it absorbs oxygen and becomes peroxide. In discharging these changes are reversed.

Another oxide, Pb_2O_3, which is precipitated as a reddish-yellow powder on the addition of sodium hydrochlorite to an alkaline lead solution, is very probably the lead salt of metaplumbic acid, H_2PbO_3:

$$Pb_2O_3 = PbPbO_3.$$

Nitric acid decomposes it into lead nitrate and peroxide. It dissolves in cold hydrochloric acid without liberation of chlorine; this gas escapes, however, when the solution is heated.

Lead Tetrachloride, $PbCl_4$, was prepared by H. Friedrich in 1893 [Monats. f. Ch. **14**, 505]. It is formed on adding lead peroxide to cold concentrated hydrochloric acid, or upon conducting chlorine into concentrated hydrochloric acid containing lead chloride in solution or in suspension. On adding ammonium chloride to the clear liquid the double salt, $PbCl_4.2NHCl$, separates in yellow isometric crystals. It is decomposed, when added to ice-cold concentrated sulphuric acid, into ammonium sulphate, hydrochloric acid and lead tetrachloride, which collects under the sulphuric acid in the form of a yellow oil.

Lead tetrachloride becomes crystalline at —15°. It decomposes gradually at the ordinary temperature into lead chloride and chlorine. The decomposition is explosive at 105°; its specific gravity at 0° is 3.18. It fumes in moist air. It is soluble in water. Concentrated solutions when warmed liberate chlorine and lead chloride separates; in dilute solutions lead peroxide is precipitated. Sodium and potassium hydroxides act similarly. The group similarity with carbon, silicon, germanium and tin expresses itself in this chloride; the chlorides of these other members are liquids at the ordinary temperature.

Lead Chloride, $PbCl_2$, separates as a white precipitate, when hydrochloric acid is added to the solution of a lead salt. It is almost insoluble in cold water; from hot water, of which it requires 30 parts for solution, it crystallizes in white, shining needles. It melts at about 500° and solidifies to a horn-like mass. It is volatile at a white heat; its vapor density corresponds to the formula $PbCl_2$.

Lead Iodide, PbI_2, is thrown down as a yellow precipitate from lead solutions by potassium iodide; it crystallizes from a hot solution in shining, yellow leaflets, melting at 383°. It is difficultly soluble in water.

Lead tetraiodide, PbI_4, and **tetrabromide**, $PbBr_4$, are known in the form of double salts with salts of organic bases (Classen and Zahorski).

Lead Nitrate, $Pb(NO_3)_2$, obtained by the solution of lead in dilute nitric acid, crystallizes in regular octahedra (isomorphous with barium nitrate) and dissolves in two parts of water at the ordinary temperature. It melts at a red heat, and is decomposed into lead monoxide, nitrogen dioxide, and oxygen. When boiled with lead oxide and water, it is converted into the basic nitrate, $Pb<\genfrac{}{}{0pt}{}{NO_3}{OH}$, which separates in white needles.

Lead Sulphate, $PbSO_4$, occurs in nature as *anglesite*, in rhombic crystals, isomorphous with barium sulphate. It is precipitated from lead solutions as a white crystalline mass by sulphuric acid. It dissolves with difficulty in water, more readily in concentrated sulphuric acid, very easily in concentrated sodium hydroxide (distinction from barium sulphate). When ignited with carbon, it is decomposed according to the following equation:

$$PbSO_4 + 2C = PbS + 2CO_2.$$

Lead Carbonate, $PbCO_3$, occurs as *cerussite* in nature. It is precipitated by ammonium carbonate from lead nitrate solutions. Potassium and sodium carbonates precipitate basic carbonates, the composition of which varies with the temperature and concentration of the solution. A similar basic salt, whose composition agrees best with the formula:

$$2PbCO_3 . Pb(OH)_2*$$

is prepared on a large scale by the action of carbon dioxide upon lead acetate. It bears the name *white lead.*

White lead was formerly manufactured by what is known as the Dutch process. Leaden plates rolled up into a spiral were moistened in earthenware pots with acetic acid, and then covered with manure and permitted to stand undisturbed for some time. In this way the action of the acetic acid and air upon the lead produced a basic acetate, which the carbon dioxide, evolved from the decaying manure, converted into basic lead carbonate. At present it is prepared by dissolving litharge in acetic acid, and converting the resulting basic acetate into a carbonate by conducting carbon dioxide into it.

White lead is employed for the manufacture of white oil colors. As it is poisonous, and blackened by the hydrogen sulphide of the air (formation of lead sulphide), it is being replaced more and more by zinc white and permanent white ($BaSO_4$).

Lead Sulphide, PbS, occurs crystallized in metallic, shining cubes and octahedra. Hydrogen sulphide precipitates it as an amorphous black powder. It is insoluble in dilute acids. Hydrogen sulphide precipitates red chloro-sulphide, $PbS . PbCl_2$, from solutions of lead salts containing much strong hydrochloric acid.

The soluble lead compounds are very poisonous. They have a sweetish, astringent taste. They are readily recognized by the following reac-

---

* Its chemical structure may be expressed by the following formula:

$$HO-Pb-CO_3-Pb-CO_3-Pb-OH.$$

tions: sulphuric acid precipitates white lead sulphate, which is soluble in sodium hydroxide; from this solution hydrogen sulphide precipitates black lead sulphide. Potassium iodide precipitates yellow lead iodide.

4. BISMUTH.

Bi = 208.5.

Bismuth constitutes a natural group with antimony, arsenic, phosphorus and nitrogen. We observed that, with increase of atomic weight, the metalloidal character of the lower members becomes more metallic; the acid nature of the oxides becomes basic. Antimony oxide (Sb_2O_3) is a base, while the higher oxide, Sb_2O_5, represents an acid anhydride. In bismuth, the metallic nature attains its full value. This is manifest in its inability to unite to a volatile compound with hydrogen and in the basic oxyhydrate BiO(OH). Bismuth trioxide is a base, and the pentoxide possesses a very feeble acid character; the latter behaves more like a metallic peroxide.

Bismuth usually occurs native, and in combination with sulphur, as *bismuthinite;* with tellurium as *tetradymite;* also as *bismuth ocher*, Bi_2O_3, and in many cobalt, nickel and silver ores.

Bismuth is obtained principally from Saxony, and in London from Bolivian and Australian ores. In Saxony the roasted ores are extracted with concentrated hydrochloric acid, and the solution then diluted with water, when the oxychloride is precipitated. It is redissolved in hydrochloric acid and freed from iron by precipitation with water, and then melted, together with coal, lime, and slag, in graphite crucibles to obtain the bismuth.

To obtain the metal, the sulphide is roasted in the air, and the resulting oxide reduced with charcoal.

Bismuth is a reddish-white metal, of specific gravity 9.9. It is brittle and may be easily pulverized. It crystallizes in rhombohedra. It fuses at 265° and distils at a white heat (about 1300°). It does not change in the air at ordinary temperatures. When heated it burns to bismuth oxide, Bi_2O_3. It is insoluble in hydrochloric acid, but dissolves in boiling sulphuric acid with formation of sulphate of bismuth, and the evolution of sulphur dioxide. Nitric acid dissolves it readily in the cold.

Water decomposes bismuth solutions in the same manner as those of antimony; insoluble basic salts are precipitated, but these are not dissolved by tartaric acid (distinction from antimony).

Bismuth Chloride, $BiCl_3$, arises from the action of chlorine upon heated bismuth, and by the solution of the metal in aqua regia. It is a white crystalline mass, which fuses at 220° and boils at about 447°. It deliquesces in the air. Water renders its hydrochloric acid solution turbid, a white, crystalline precipitate of *bismuth oxychloride*, BiOCl, separating at the same time:

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

The metalloidal character of bismuth is indicated by this reaction.

The compounds $BiBr_3$ (orange-yellow) and BiI_3 (black or dark brown) are very similar to bismuth chloride. All three combine with many metallic haloid salts to form double halogen derivatives.

Halogen derivatives of quinquivalent bismuth are unknown.

Bismuth Oxide, Bi_2O_3, prepared by burning bismuth or heating the nitrate, is a yellow powder, insoluble in water and the alkalies.

Normal **bismuth hydroxide,** $Bi(OH)_3$, is not known in a free state. Potassium hydroxide added to a bismuth solution precipitates a white amorphous *metahydrate*, $BiO.OH$.

Chlorine conducted through a concentrated potassium hydroxide solution in which bismuth oxide is suspended precipitates red **bismuthic acid** ($HBiO_3$ or $H_2Bi_2O_6$), which, when gently heated, becomes Bi_2O_5, *bismuthic oxide.* Strong ignition converts the latter into bismuth trioxide and oxygen; hydrochloric acid dissolves it to bismuth chloride, with liberation of chlorine.

Bismuth Nitrate, $Bi(NO_3)_3$, is obtained by the solution of bismuth in nitric acid, and crystallizes with five molecules of water in large, transparent tables. In a little water it dissolves without any change; much water renders it turbid, owing to the precipitation of white, curdy basic salts: $Bi\left\{\begin{matrix}NO_3\\NO_3\\OH\end{matrix}\right.$ and $Bi\left\{\begin{matrix}NO_3\\OH\\OH\end{matrix}\right.$. The precipitate is employed in medicine under the name of *Bismuthum subnitricum* (*subnitrate*). It frequently contains tellurium.

Bismuth Sulphate, $Bi_2(SO_4)_3$, is formed when bismuth dissolves in sulphuric acid. It crystallizes in delicate needles. **Bismuth Sulphide,** Bi_2S_3, occurring as bismuthinite, is thrown down as a black precipitate from bismuth solutions by hydrogen sulphide. Unlike antimony and arsenic sulphides, it does not form sulpho-salts.

The alloys of bismuth are nearly all readily fusible. An alloy of 4 parts of bismuth, 1 part of cadmium, 1 part of tin, and 2 parts of lead, fuses at 65° (Wood's metal). The alloy of 9 parts of bismuth, 1 part of lead and 1 part of tin (Rose's metal) fuses at 94°.

Alkaline stannous solutions precipitate metallic bismuth from solutions of its salts:

$$2BiO.OH + 3K_2SnO_2 = 2Bi + 3K_2SnO_3 + H_2O.$$

CHROMIUM GROUP.

We observed that a group of more metallic analogous elements: titanium, zirconium and thorium attached itself to the metalloidal elements, carbon, silicon and tin (p. 238); and further that their was an analogous group of more metallic elements: vanadium, niobium and tantalum, corresponding to the metalloidal group of phosphorus (p. 226). We now meet a group of metals, consisting of chromium, molybdenum, tungsten, and probably uranium, that bears a like relation to the elements of the sulphur group (see Periodic System of the Elements). The resemblance of these elements to sulphur and its analogues is plainly manifest in their highest oxygen compounds XO_3, and their derivatives (see also Manganese). As the elements of the sulphur group in their highest oxygen compounds are sexivalent, so chromium, molybdenum, tungsten and uranium form acid oxides: CrO_3, MoO_3, WO_3, UO_3. Many of the salts corresponding to these are very similar to and isomorphous with the salts of sulphuric acid. Sodium chromate, like sodium sulphate, crystallizes with ten molecules of water; the potassium salts of both groups form isomorphous mixtures; their magnesium salts, as well as that of tungstic acid, have the same constitution:

$$MgSO_4 + 7H_2O \text{ and } MgCrO_4 + 7H_2O.$$

Corresponding to the acid oxides are the chlorine derivatives:

$$SO_2Cl_2, CrO_2Cl_2, MoO_2Cl_2, MoOCl_4, WOCl_4 \text{ and } WCl_6,$$

which are perfectly analogous, so far as chemical deportment is concerned.

The most important basic oxide of chromium is its sesquioxide. This affords salts with the acids, and they are perfectly similar to those of the sesquioxides of iron (Fe_2O_3), manganese (Mn_2O_3), and aluminium (Al_2O_3) (p. 330).

Finally, compounds of chromium, $\overset{\text{II}}{Cr}X_2$, are known in which the metal figures as a dyad. These so-called *chromous* compounds are very unstable, and are oxidized by the air into chromic compounds. In this respect they also resemble the ferrous derivatives FeX_2 (p. 398).

Chromium compounds containing more oxygen than the chromates are found in the salts of *perchromic acid;* however, nothing definite is known of their constitution at present. The same is true of tungsten and molybdenum (pp. 381, 383, 384).

Salts of molybdenum and tungsten, corresponding to the states of lowest oxidation, are not known, because these metals occur as hexads in most of their derivatives. Uranium, which has the highest atomic weight of the group, shows some variations from its analogues.

1. CHROMIUM.

$Cr = 52.1.$

Chromium is found principally as chromite in nature. This is a combination of chromic oxide with ferrous oxide, $Cr_2O_3 . FeO$, and occurs in North America, Sweden, Hungary, and in large quantities in the Urals. Crocoisite, or lead chromate ($PbCrO_4$), is not met with so frequently. Chromite is used almost exclusively for the preparation of all other chromium derivatives, as it is first converted into potassium chromate by fusion with potassium carbonate and nitrate (p. 379).

Metallic chromium was first obtained free from carbon and fused in large quantities in 1898 by Goldschmidt, who ignited a mixture of chromic oxide and aluminium powder (p. 347):

$$Cr_2O_3 + Al_2 = Al_2O_3 + Cr_2.$$

It is bright gray in color, very brilliant, and on cleavage faces shows strong crystallization. It is very hard, extremely difficult to melt and very stable in the air. W. Hittorf claims that chromium behaves like a noble metal at the ordinary temperature in that it is inactive electromotively and in the tension series arranges itself with platinum. Hydrochloric acid at 0° has no action upon it and when it is made the anode it dissolves in the acid as chromic acid. At more elevated temperatures it decomposes hydrochloric acid with the liberation of hydrogen; and in an electromotive respect follows zinc. It dissolves as chromous chloride.

Four series of chromium compounds are known: *chromous* (CrX_2), *chromic* (CrX_3), the derivatives of chromic acid, called *chromates*, and the *perchromates*. All chromium compounds are brightly colored, hence the name chromium (from χρῶμα, color).

CHROMOUS COMPOUNDS.

These are very unstable, and by oxidation pass readily into chrom*ic* compounds. Like ferrous salts, they are produced by the reduction of the higher oxides. The following may be mentioned: **Chromous Chloride**, $CrCl_2$. This is obtained by heating chromic chloride, $CrCl_3$, in a stream of hydrogen or by dissolving chromium in hydrochloric acid. It is a white crystalline powder. It volatilizes without decomposition. At 1300-1600° the vapor density corresponds to a mixture of the molecules $CrCl_2$ and Cr_2Cl_4. It dissolves in water with a blue color; the solution absorbs oxygen with avidity, and becomes green in color [Ann. Chem. **228** (1885), 113]. The alkalies precipitate yellow **chromous hydroxide**, $Cr(OH)_2$, from it. This is readily oxidized. When heated it parts with hydrogen and water and becomes chromic oxide:

$$2Cr(OH)_2 = Cr_2O_3 + H_2 + H_2O.$$

CHROMIC COMPOUNDS.

Chromic Chloride, $CrCl_3$, like $AlCl_3$, is obtained by ignition of the oxide and charcoal or, better, the metal in a current of chlorine. When raised to a red heat in this condition it sublimes in shining violet leaflets, which are transformed into chromic oxide by ignition in the air. Its vapor density at 1200–1300° corresponds to the formula $CrCl_3$; it vaporizes very slowly below 1000°.

Pure chromic chloride only dissolves in water after long-continued boiling; if, however, it contains traces of chromous chloride, $CrCl_2$, it dissolves readily at ordinary temperatures. Green crystals of $CrCl_3 + 6H_2O$ separate from the green solution on evaporation; these deliquesce in the air. The same crystals may be obtained from solutions of chromic hydroxide, $Cr(OH)_3$, in hydrochloric acid. When they are dried intermediate oxychlorides, $CrCl_2(OH)$ and $Cr_2Cl(OH)_2$, are formed; finally $Cr(OH)_3$ remains.

Chromic Hydroxide, $Cr(OH)_3$. It is precipitated by ammonium hydroxide from chromic solutions as a voluminous bluish gray, hydrous mass. The green precipitates produced by sodium and potassium hydroxides contain alkali that cannot be removed even by boiling water. They dissolve readily with an emerald-green color, in an excess of potassium or sodium hydroxide (slightly in ammonia), but they are reprecipitated upon boiling their solutions. When chromic hydroxide is heated to 200° in a current of hydrogen, the product is the hydroxide, $CrO.OH$, which is a grayish-blue powder, insoluble in dilute hydrochloric acid.

Chromic Oxide, Cr_2O_3, is a green, amorphous powder. It is also formed by the ignition of chromium trioxide:

$$2CrO_3 = Cr_2O_3 + 3O,$$

or of ammonium dichromate:

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2.$$

It may be obtained in black, hexagonal crystals, by conducting the vapors of the oxychloride (p. 380) through a tube heated to redness:

$$2CrO_2Cl_2 = Cr_2O_3 + 2Cl_2 + O.$$

Ignited chromic oxide is insoluble in acids. When fused with silicates, it colors them emerald-green, and serves, therefore, to color glass and porcelain.

Guignet's green is a beautifully green-colored chromium hydroxide, which is applied as a paint. It is obtained by igniting a mixture of one part of potassium dichromate with three parts of boric acid; after treating the mass with water, which dissolves potassium borate, there remains a green powder, the composition of which corresponds to the formula:

$$Cr_2O(OH)_4.$$

The predominating properties of chromic oxide are basic, as it readily affords salts with acids; yet its basic nature, like that of all sequioxides, is but slight, so that it does not afford salts with weak acids (p. 374). In addition to all this it possesses a slightly acidic character, and metallic salts are derived from it, generally from the hydroxide, $CrO.OH$, which are analogous to the aluminates (p. 351). Such salts—*chromites*—like $(CrO.O)_2Mg$ and $(CrO.O)_2Zn$, can be obtained crystallized in regular octahedra by fusing chromic oxide with metallic oxides and boron trioxide (as flux). The mineral chromite is such a salt:

$$Cr_2O_3.FeO = (CrO.O)_2Fe.$$

Chromium Sulphate, $Cr_2(SO_4)_3$, is obtained by dissolving the hydroxide in concentrated sulphuric acid. The solution, green at first, becomes violet on standing, and deposits a violet-colored crystalline mass. This may be purified by solution in water and precipitation by alcohol. This salt crystallizes from very dilute alcohol in bluish-violet octahedra containing fifteen molecules of water. If the aqueous solution of the violet salt be heated, it assumes a green color, because the salt breaks down into free acid and a basic salt which, upon evaporation, separates as a green amorphous mass, soluble in alcohol. When the green solution stands, it reverts to the violet of the neutral salt. The other chromic salts, the nitrate and the alum, behave in a similar manner.

It is very probable that in the green solutions the chromium exists as a part of peculiar "complex" acids: chrom-sulphuric acid, chrom-nitric acid; it no longer appears as ion, but as a part of the latter. Hence the salts of green solutions do not show the reactions of salts of chromic oxide nor of sulphuric acid.

Chromium sulphate forms double salts with the alkaline sulphates—the chromium alums (p. 352).

Potassium Chromium Alum, $K_2SO_4 . Cr_2(SO_4)_3 + 24H_2O$, crystallizes in large, dark-violet octahedra. It is most conveniently prepared by conducting sulphur dioxide through a solution of potassium dichromate containing sulphuric acid:

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = Cr_2(SO_4)_3 . K_2SO_4 + H_2O.$$

At 80° the violet solution of the salt becomes green, and on evaporation yields an amorphous green mass.

As chromium hydroxide possesses only a slightly basic nature, salts with weak acids, like carbonic, sulphurous, and hydrosulphuric acids (see Aluminium, p. 325) do not exist. Therefore, the alkaline carbonates and sulphides precipitate chromium hydroxide from solutions of chromium salts:

$$Cr_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 2Cr(OH) + 3Na_2SO_4 + 3CO_2$$

and

$$Cr_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = 2Cr(OH)_3 + 3(NH_4)_2SO_4 + 3H_2S.$$

Ammonium sulphide produces a black precipitate, chromous sulphide, CrS, in solutions of chromous salts.

DERIVATIVES OF CHROMIC ACID.

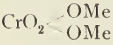
In its highest oxygen derivative, CrO_3, chromium possesses a complete metalloidal, acid-forming character. Chromic acid, H_2CrO_4, is perfectly analogous to sulphuric acid, H_2SO_4, but has not been obtained free, since when liberated from its salts it at once breaks down into the oxide and water:

$$H_2CrO_4 = CrO_3 + H_2O.$$

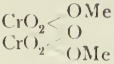
The chromates are often isomorphous with the corresponding sulphates (p. 379). *Polychromates* also exist, and are derived from polychromic acids produced by the condensation of several molecules of the normal acid (see Disulphuric Acid, p. 193):

H_2CrO_4,	$H_2Cr_2O_7$,	$H_2Cr_3O_{10}$, etc.
Chromic acid.	Dichromic acid.	Trichromic acid.

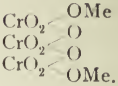
The constitution of their salts is expressed by the following formulas:



$$CrO_2<\begin{matrix}OMe\\OMe\end{matrix}$$



$$\begin{matrix}CrO_2<\\CrO_2<\end{matrix}\begin{matrix}OMe\\O\\OMe\end{matrix}$$



$$\begin{matrix}CrO_2<\\CrO_2<\\CrO_2<\end{matrix}\begin{matrix}OMe\\O\\O\\OMe.\end{matrix}$$

The free polychromic acids are not known, because as soon as they are separated from their salts, they immediately break down into the acid oxide and water:

$$H_2Cr_3O_{10} = 3CrO_3 + H_2O.$$

The polychromates are frequently, but incorrectly, called *acid* salts; true acid or primary salts, in which only one hydrogen atom is replaced by metal ($KHCrO_4$), are unknown for chromic acid.

The salts of normal chromic acid are mostly yellow colored, while the polychromates are red. The latter are produced from the former by the action of acids:

$$2K_2CrO_4 + 2HNO_3 = K_2Cr_2O_7 + 2KNO_3 + H_2O.$$

Conversely, by the action of the alkalies, the polychromates pass into the normal salts:

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

The formation of the polychromates may be explained as follows: The chromic acid liberated from its salts by stronger acids breaks down into water and the acid oxide, which combines with the excess of the normal chromate:

$$K_2CrO_4 + CrO_3 = K_2Cr_2O_7.$$

When there is an excess of acid the anhydride (CrO_3) is set free.

Chromium Trioxide, or *Chromic acid anhydride* (*Acidum chromicum*), CrO_3, consists of long, red, rhombic needles or prisms, obtained by adding sulphuric acid to a concentrated potassium dichromate solution. The crystals are readily soluble in water and deliquesce in the air if not perfectly free from sulphuric acid. When heated, they blacken, melt, and at about 250° decompose into chromic oxide and oxygen:

$$2CrO_3 = Cr_2O_3 + 3O.$$

It volatilizes without decomposition in slight quantities and this even occurs below its point of fusion.

Chromium trioxide is a powerful oxidizing agent, and destroys organic matter; hence its solution cannot be filtered through paper. When alcohol is poured on the crystals, detonation takes place, the alcohol burns, and green chromic oxide remains. By the action of acids, *e. g.*, sulphuric, the trioxide deports itself like a peroxide; oxygen escapes and a chromic salt results. When heated with concentrated hydrochloric acid chlorine is evolved:

$$2CrO_3 + 12HCl = Cr_2Cl_6 + 6H_2O + 3Cl_2.$$

Reducing substances, like sulphurous acid and hydrogen sulphide, convert chromic acid into oxide:

$$2CrO_3 + 3H_2S = Cr_2O_3 + 3H_2O + 3S,$$
$$2CrO_3 + 3SO_2 + 3H_2O = Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O.$$

Alcohol acts similarly, being oxidized to aldehyde:

$$2CrO_3 + 3H_2SO_4 + 3C_2H_6O = Cr_2(SO_4)_3 + 6H_2O + 3C_2H_4O.$$

Potassium Chromate, K_2CrO_4, is obtained by adding potassium hydroxide to potassium dichromate. It forms yellow rhombic crystals, isomorphous with potassium sulphate (K_2SO_4); isomorphous mixtures crystallize out from the solution of the two salts.

Neutral alkali chromates are always produced when any chromium compound is fused with an alkaline carbonate and some oxidizing agent (saltpeter, potassium chlorate). The addition of the oxidant is unnecessary if the oxygen of the air can act sufficiently upon the fusion. Chromic iron ore is roasted in reverberatory furnaces with soda and lime. Neutral sodium chromate, ferric oxide, and calcium carbonate are the products:

$$2Cr_2O_3.FeO + 4Na_2CO_3 + 4CaO + 7O = 4Na_2CrO_4 + 4CaCO_3 + Fe_2O_3.$$

The neutral chromate is extracted with water. When this solution is concentrated and mixed with sulphuric acid anhydrous sodium sulphate separates even from the hot liquid, from which, on further evaporation, **Sodium Dichromate,** $Na_2Cr_2O_7 + 2H_2O$, deposits in red crystals on cooling:

$$2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O.$$

All other chromium preparations are made from this salt [see Häussermann, Jahrb. f. Ch. (1891), 1, 327]. Chromates are also produced if chromium or its alloys are made the anode in an alkaline bath.

Potassium Dichromate, or *Bichromate of potash*, $K_2Cr_2O_7$, called acid potassium chromate, is manufactured on a large scale by transposing the sodium salt with potassium chloride:

$$Na_2Cr_2O_7 + 2KCl = K_2Cr_2O_7 + 2NaCl.$$

The great difference in solubility in water renders the separation of the sodium chloride and potassium dichromate an easy matter.

Potassium dichromate (called *red chromate of potash* in commerce) crystallizes in large, red, triclinic prisms, soluble at ordinary temperatures, in ten parts of water. When heated, the salt fuses without change; at a very high heat it decomposes into potassium chromate, chromic oxide, and oxygen:

$$2K_2Cr_2O_7 = 2K_2CrO_4 + Cr_2O_3 + 3O.$$

When the salt is warmed with sulphuric acid, oxygen escapes and potassium chromium alum is produced:

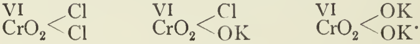
$$K_2Cr_2O_7 + 4H_2SO_4 = Cr_2(SO_4)_3 . K_2SO_4 + 4H_2O + 3O.$$

This reaction answers for the preparation of perfectly *pure oxygen.* Further, the mixture is made use of in laboratories, as an oxidizing agent.

Sodium Chromate, $Na_2CrO_4 + 10H_2O$, forms deliquescent crystals, and is analogous to Glauber's salt ($Na_2SO_4 + 10H_2O$). **Barium** and **Strontium Chromates**, $BaCrO_4$ and $SrCrO_4$, are almost insoluble in water. **Calcium Chromate**, $CaCrO_4$, dissolves with difficulty in water, and crystallizes like gypsum with two molecules of water. The *magnesium salt*, $MgCrO_4 + 7H_2O$, dissolves readily and corresponds to Epsom salts, $MgSO_4 + 7H_2O$. The chromates of the heavy metals are insoluble in water, and are obtained by transposition.

Lead Chromate, $PbCrO_4$, is obtained by the precipitation of soluble lead salts with potassium chromate. It is a yellow amorphous powder which serves as a yellow paint—*chrome yellow.* When heated it melts undecomposed, and solidifies to a brown, radiating crystalline mass. It oxidizes all the carbon compounds at a red heat, and is therefore used in their analysis. In nature lead chromate exists as crocoisite.

Chromic Acid Chloranhydrides.—Chromic acid forms chloranhydrides similar to those of sulphuric acid (p. 195). Corresponding to sulphuryl chloride, SO_2Cl_2, we have chromyl chloride, CrO_2Cl_2; and for the first sulphuric acid chloranhydride, $SO_2\left\{\begin{matrix}Cl\\OH\end{matrix}\right.$, is the salt, $CrO_2\left\{\begin{matrix}Cl\\OK\end{matrix}\right.$:



$$\overset{VI}{Cr}O_2<\begin{matrix}Cl\\Cl\end{matrix} \qquad \overset{VI}{Cr}O_2<\begin{matrix}Cl\\OK\end{matrix} \qquad \overset{VI}{Cr}O_2<\begin{matrix}OK\\OK\end{matrix}.$$

Chromyl Chloride, CrO_2Cl_2, *Chromium oxychloride,* is produced by heating a mixture of potassium (or sodium) dichromate (or monochromate) and sodium chloride with sulphuric acid:

$$Na_2CrO_4 + 2NaCl + 4H_2SO_4 = CrO_2Cl_2 + 4NaHSO_4 + 2H_2O,$$

and

$$Na_2Cr_2O_7 + 4NaCl + 6H_2SO_4 = 2CrO_2Cl_2 + 6NaHSO_4 + 3H_2O.$$

The water produced at the same time must be absorbed by the excess of sulphuric acid.

To prepare chromyl chloride, first fuse salt (10 parts) with potassium dichromate (12 parts) or with potassium monochromate (17 parts). The yellowish-brown mass is broken into coarse pieces, placed in a retort provided with a condenser, and anhydrous or slightly fuming sulphuric acid (30 parts) poured over them. When a gentle heat is applied chromyl chloride distils over and is purified by further distillation.

Chromyl chloride is a red, transparent liquid, of specific gravity 1.91 at 25°, and fumes strongly in the air. It boils at 116–118°; its vapor density corresponds to the molecular formula CrO_2Cl_2.

With water it is decomposed according to the following equation:

$$CrO_2Cl_2 + H_2O = CrO_3 + 2HCl.$$

Chloro-chromic Acid, $CrO_2{<}^{Cl}_{OH}$ (see p. 380), is only known in its salts. The potassium salt is formed by heating potassium dichromate (3 parts) for a short period, with concentrated hydrochloric acid (4 parts):

$$K_2Cr_2O_7 + 2HCl = 2CrO_2{<}^{Cl}_{OK} + H_2O.$$

It crystallizes from the solution on cooling in flat, red needles. Heated to 100° it gives up chlorine. It is decomposed by water into hydrochloric acid and potassium dichromate:

$$2CrO_2{<}^{Cl}_{OK} + H_2O = K_2Cr_2O_7 + 2HCl.$$

Bromides and iodides of chromic acid are not known, but **Chromyl Fluoride,** CrO_2Fl_2, a red-colored and very volatile liquid, which is decomposed by water with the formation of chromic and hydrofluoric acids, is obtained by heating a mixture of lead chromate and calcium fluoride with concentrated sulphuric acid in platinum or lead vessels. It etches glass. It was formerly thought to be chromium hexafluoride, $CrFl_6$.

The following reaction is very characteristic for chromic acid: On adding hydrogen peroxide to a solution of chromium trioxide, or the acidified solution of a chromate, the red liquid is colored blue. On shaking the blue solution with ether, the latter withdraws the blue compound which O. F. Wiede [Ber. 31 (1898), 516] considers to be the **anhydride of perchromic acid,** Cr_2O_9, together with hydrogen peroxide. This chemist succeeded in preparing alkali salts of the perchromic acid but always combined with hydrogen peroxide. They are violet in color and are readily decomposed; their formula is probably

$$MeO.CrO_4 + H_2O_2,$$

and that of the hypothetical acid:

$$CrO_4.OH.$$

They lose oxygen and become dichromates. Silver nitrate produces a brownish-red precipitate of *silver chromate,* Ag_2CrO_4, with aqueous solutions of the chromates. This silver salt dissolves very readily in ammonia and in the mineral acids.

2. MOLYBDENUM.

Mo = 96.0.

Molybdenum is of comparatively rare occurrence in nature; usually as molybdenite (MoS_2) and wulfenite ($PbMoO_4$). Scheele, in 1778, obtained molybdic acid from molybdenite which had until then been considered graphite. Hjelm, in 1790, prepared molybdenum as a silver-white metal, of specific gravity 8.6, by igniting the chlorides or oxides in a stream of hydrogen. It is very hard, fuses at a higher temperature than platinum, and is as ductile and as susceptible of polish as iron. Like the latter it takes up carbon at 1500° and becomes so hard that it will scratch glass. When heated in the air it oxidizes to molybdenum trioxide. It is soluble in concentrated sulphuric and nitric acids. It is also converted by the latter into insoluble molybdenum trioxide, MoO_3.

Molybdenum forms derivatives of the most different types, so that it is apparently a bivalent, trivalent, quadrivalent, etc., and even an octivalent metal. The vapor density of its chloride, $MoCl_5$, has been determined and in it the metal is positively quinquivalent. In its most stable oxide, MoO_3, it is apparently sexivalent and in the stable sulphide MoS_2 quadrivalent; but we are ignorant as to the constitution of these bodies as well as of their molecular magnitudes. Only the most important will be described.

Molybdenum Dichloride, $MoCl_2$, resulting from the trichloride, $MoCl_3$, when heated in a stream of carbon dioxide (together with $MoCl_4$), is a bright yellow, non-volatile powder. It is converted by potassium hydroxide into the hydrate, $Mo(OH)_2$, a black powder.

The molecular formula of this chloride (and that of the corresponding bromide) must apparently be trebled—Mo_3Cl_6, because dilute alkalies change it to *chloromolybdic hydroxide*, $Cl_4Mo_3(OH)_2$. The latter behaves like a diacid base having the radical $(Mo_3Cl_4)^{II}$. Concentrated haloid acids convert it into salts of the formula $(Mo_3Cl_4)R_2$, in which only the two R-halogen atoms are precipitated by silver nitrate. In the chloride $(Mo_3Cl_4)Cl_2$ therefore only two chlorine atoms are precipitated as silver chloride. On the other hand, chloromolybdic hydroxide (a bright yellow amorphous powder) is also a feeble acid. It dissolves without change in dilute alkalies and is reprecipitated from its yellow solution by weak acids.

The iron cyanide radical $[Fe(CN)_6]$ and many other radicals containing halogens, derived from cobalt, chromium and platinum, conduct themselves like (Mo_3Cl_4). In these compounds, the halogens belonging to the radicals are obscured—protected—from the reagents with which we are accustomed to see them react in their hydrogen and other derivatives. This is true also of the other parts of the radicals, of the molybdenum in (Mo_3Cl_4), of the iron in $[Fe(CN)_6]$, etc., etc. These metals can be no longer recognized by the reagents with which they are ordinarily detected. These new relations and their explanation, by the theory of electrolytic dissociation, will be again considered in connection with the iron-cyanogen compounds.

Molybdenum Trichloride, $MoCl_3$, produced by gentle heating (at 250°) of molybdenum pentachloride, $MoCl_5$, in a current of hydrogen or carbon dioxide, is a reddish-brown powder, resembling red phosphorus, which, when strongly ignited, yields a dark-blue vapor. It dissolves with a beautiful blue color in concentrated sulphuric acid, upon heating, with an emerald-green color. Potassium hydroxide converts it into the *hydroxide*, $Mo(OH)_3$, which forms salts with acids. The ignition of the hydrate affords the black oxide, Mo_2O_3. Strong heating of the trichloride in a current of carbon dioxide leaves molybdenum dichloride, $MoCl_2$, and it sublimes.

Molybdenum Tetrachloride, $MoCl_4$, is a brown, crystalline powder, which appears to break up by evaporation into pentachloride, $MoCl_5$, and trichloride, $MoCl_3$. *Molybdenum disulphide*, MoS_2, is produced by the ignition of the *trisulphide*, MoS_3, away from air. It is a shining black powder, which occurs native as *molybdenite*, in hexagonal, graphite-like crystals, with a specific gravity of 4.6.

Molybdenum Pentachloride, $MoCl_5$, is prepared by heating molybdenite (MoS_2), or molybdenum in dry chlorine gas. It is a metallic, shining, black, crystalline mass, fusing at 194° and distilling at 268°; its vapor density corresponds to the molecular formula $MoCl_5$. It fumes and deliquesces in the air, and dissolves in water with hissing.

Its aqueous solution has a brown color. It dissolves in absolute alcohol and ether with a dark-green color.

The *hexachloride*, $MoCl_6$, is not known, but the *oxychlorides*, $MoOCl_4$, and MoO_2Cl_2, are.

Bromine forms perfectly analogous compounds with molybdenum.

Molybdenum Trioxide, MoO_3, results on roasting metallic molybdenum or the sulphide in the air. It is a white, amorphous mass, which turns yellow on heating; it fuses at a red heat and then sublimes in brilliant rhombic plates and needles. It is insoluble in water and acids; but dissolves readily in the alkalies and ammonium hydroxide. When fused with the alkaline hydroxides or carbonates, salts are produced, partly derived from the normal acid, H_2MoO_4, and partly from the poly-acids, and correspond to the polychromates:

$$K_2MoO_4, \quad K_2Mo_2O_7, \quad K_2Mo_3O_{10}, \quad Na_2Mo_4O_{13}, \quad K_6Mo_7O_{24}, \text{ etc.}$$

The *ammonium salt*, $(NH_4)_2MoO_4$, is obtained by dissolving the trioxide in concentrated ammonium hydroxide. In the laboratory it serves as a reagent for phosphoric acid. Alcohol causes it to separate out of its solution in crystals; upon evaporation, however, the salt, $(NH_4)_6Mo_7O_{24} + 4H_2O$, crystallizes out. Both salts are decomposed by heat, leaving molybdenum trioxide.

Nitric acid gradually separates a yellow crystalline powder from the alkali molybdates, $MoO(OH)_4$, which is only slightly soluble in water. It loses water on drying and changes to the normal hydrate **Molybdic Acid**, H_2MoO_4. By the action of reducing agents, such as zinc, stannous chloride, and sulphur dioxide, molybdic acid solutions are colored first blue, then green, then brownish-red, and finally brown. This is due to the formation of different lower oxides. The first blue-colored reduction product is formed by warming a molybdic acid solution with metallic molybdenum; it has the formula Mo_3O_8 ($= 2MoO_3 . MoO_2$). The final product, by the action of tin and hydrochloric acid, is molybdenum sesquioxide, Mo_2O_3. Its compounds are usually yellow in color. Potassium permanganate converts all these lower oxides into molybdic acid.

Hydrogen peroxide converts molybdic acid and its salts into derivatives richer in oxygen; these were supposed to be derived from a *permolybdic acid*, $HMoO_4$. The latest researches have demonstrated that their oxygen content varies and that they cannot be referred to a common parent body. It is thought that they contain, like ozone and hydrogen peroxide, oxygen atoms $= O_2$ in union with one another, therefore they have been designated *ozomolybdates* (Muthmann and Nagel, Ber. **31** (1898), 1836).

Molybdic acid can also form poly-acids with phosphoric and arsenic acids, *e. g.*, $H_3PO_4 . 11MoO_3$. These complex phosphomolybdic acids are distinguished by the fact that they form salts insoluble in dilute acids with the metals of the potassium group, with ammonia, with thallium and with organic bases. Sodium and lithium salts do not yield precipitates with these acids. On adding a solution containing phosphoric (or arsenic) acid to the nitric acid solution of ammonium molybdate, there is produced a yellow crystalline precipitate of ammonium phospho-molybdate, $(NH_4)_3PO_4 . 11MoO_3 + 6H_2O$. This reaction serves for the detection and separation of phosphoric acid.

Molybdenum Trisulphide, MoS_3, is thrown down as a brown precipitate from acidulated molybdenum solutions by hydrogen sulphide. It dissolves in alkaline sulphides forming sulpho-salts. Ignited away from air it is converted into black molybdenum disulphide, MoS_2, which occurs native as molybdenite.

In addition to these molybdenum compounds in which the element is sexivalent there is a

Molybdenum Tetrasulphide, MoS_4. From this are derived persulphomolybdic acid, H_2MoS_5, and its salts, *e. g.*, K_2MoS_5 and $KHMoS_5$.

3. TUNGSTEN.

$W = 184$.

Tungsten is found in nature in the tungstates: as wolframite, $(Fe,Mn)WO_4$, as scheelite, $CaWO_4$, and as stolzite, $PbWO_4$.

The metal is obtained, like molybdenum, by the ignition of the oxides or chlorides in a stream of hydrogen, in the form of a black powder, or in steel-gray crystalline leaflets, having a specific gravity of 19. It is very hard and difficultly fusible. It becomes trioxide when ignited in the air.

Tungsten forms the following chlorides: WCl_2, WCl_4, WCl_5 and WCl_6.

The **Pentachloride**, WCl_5, is obtained by the distillation of WCl_6 in a current of hydrogen or carbon dioxide, and consists of shining, black, needle-like crystals. It melts at 248° and boils at 275°, forming a greenish-yellow vapor, with the density 360 ($WCl_5 = 361.25$; $O_2 = 32$). It affords an olive-green solution and a blue oxide, W_2O_5, with water. It dissolves with a deep-blue color in carbon bisulphide.

Tungsten Hexachloride, WCl_6, is produced when the metal or a mixture of wolframite with carbon is heated in a current of chlorine. It forms a dark-violet, crystalline mass, which melts at 275° and boils at 346°. The vapor density corresponds to the formula WCl_6. It dissolves in carbon bisulphide with a reddish-brown color; it forms tungsten trioxide, WO_3, with water. The other chlorides are obtained from it by heating them alone or in a current of hydrogen gas.

The **Oxychloride**, $WOCl_4$, consists of red crystals, fusing at 210° and boiling at 229°; its vapor density equals 340 ($WOCl_4 = 341.8$). The **Dioxychloride**, WO_2Cl_2, sublimes in bright yellow, shining leaflets. They are produced from the other chlorides by the action of water.

Tungsten Trioxide, WO_3, is thrown out of the hot solution of tungstates by nitric acid, as a yellow precipitate, insoluble in acids, but dissolving readily in potassium and sodium hydroxides. **Tungstic Acid**, $WO(OH)_4$, is, however, precipitated from the cold solution, but on standing over sulphuric acid it becomes $WO_2(OH)_2$ and at 100° passes into ditungstic acid, $H_2W_2O_7 = W_2O_5(OH)_2$.

When tungstic acid is reduced in hydrochloric acid solution by zinc it first becomes blue (formation of W_2O_5), and then brown, when the salt of the dioxide, WO_2, is formed. Potassium permanganate oxidizes this to tungstic acid.

The salts of tungstic acid are perfectly analogous to the molybdates, and are derived from the normal acid or the poly-acids. The *normal sodium salt*, $Na_2WO_4 + 2H_2O$, and the so-called *sodium meta-tungstate*, $Na_2W_4O_{13} + 10H_2O$, are applied practically. Materials saturated with their solutions do not burst into a flame, but smoulder away slowly.

Tungstic acid and the tungstates behave toward hydrogen peroxide just like molybdic acid.

The reduction of the alkaline tungstates (by fusion with tin, etc.) affords peculiar compounds, *e. g.*, $K_2W_4O_{12}$ or $Na_x(WO_3)_y$; these have various colors, possess metallic luster, and are applied as tungsten bronzes.

Tungstic acid also combines with phosphoric and arsenic acids, forming derivatives analogous to those of molybdic acid with the same acids.

The metal is used in the manufacture of tungsten steel; a slight quantity of it increases the hardness of the latter very considerably. It was first prepared in 1783 by J. and F. d'Elhujar.

4. URANIUM.

$U = 239.5$.

In nature it occurs chiefly as uraninite, a compound of uranic and uranous oxides, $UO_2 . 2UO_3 = U_3O_8$.

The metal, first obtained in 1840 by Péligot on heating uranous chloride with sodium, has a silver-white color and a specific gravity of 18.7. When heated in the air it burns to uranous-uranic oxide. Its specific heat equals 0.0267, and its atomic volume is therefore

6.6. It melts at about 1500°. There are two series of uranium compounds. In the one, the metal is a tetrad UX_4; these uranous or urano-compounds are very unstable, and pass readily into the uranic or derivatives of sexivalent uranium. Uranous oxide is of a basic nature, and only forms salts with acids.

The compounds of sexivalent uranium are called the uranic compounds. The oxide, UO_3, and the hydroxide, $UO_2(OH)_2$, have a predominant basic character, but are also capable of forming salts with bases which are called *uranates*. In the salts derived from acids, *e. g.*, $UO_2(NO_3)_2$ and $UO_2 . SO_4$, the group UO_2 plays the rôle of a metal; it is called *uranyl*, and its salts are termed *uranyl salts*. They may also be regarded as basic salts.

URANOUS COMPOUNDS.

Uranous Chloride, UCl_4, is obtained by heating metallic uranium in a stream of chlorine, or uranous oxide in hydrochloric acid. It consists of dark-green octahedra with metallic luster. It volatilizes at a red heat, forming a red vapor, whose density agrees with the formula UCl_4. It deliquesces in the air, and dissolves with hissing in water. Uranous hydroxide remains when the solution is evaporated.

Uranous Oxide, UO_2, is formed when the other oxides are heated in a current of hydrogen. It is a black powder, which becomes uranous-uranic oxide, $UO_2 . 2UO_3$, when heated in the air.

Uranous oxide dissolves with a green color in hydrochloric and concentrated sulphuric acids. *Uranous sulphate*, $U(SO_4)_2 + 8H_2O$, consists of green crystals. From the salts the alkalies precipitate the voluminous, bright green *uranous hydroxide*, $U(OH)_4$, which becomes brown on exposure. Uranous salt solutions are distinguished by a very remarkable absorption spectrum.

SEXIVALENT URANIUM COMPOUNDS.

Uranium Hexachloride, UCl_6, has not been obtained, but the **oxychloride,** UO_2Cl_2 (uranyl chloride), exists; it is made by heating UO_2 in dry chlorine gas, or by the evaporation of uranyl nitrate with hydrochloric acid. It is a yellow crystalline mass, deliquescing in the air.

Uranic Oxide, UO_3 or **Uranyl Oxide,** $UO_2 . O$, is a yellow powder, and is obtained by heating uranyl nitrate to 250°. When warmed with nitric acid it becomes *uranyl hydrate* or *uranic acid*, $UO_2(OH)_2$, which is also yellow-colored.

Uranyl Nitrate, $UO_2(NO_3)_2$, results from the solution of uranous or uranic oxide, or more simply of uraninite in nitric acid. It crystallizes with six molecules of water, in large, greenish-yellow prisms, which are readily soluble in water and alcohol. On adding sulphuric acid to the solution, **Uranyl Sulphate,** $UO_2SO_4 + 6H_2O$, crystallizes out, on evaporation, in lemon-yellow needles.

If sodium or potassium hydroxide be added to the solutions of uranyl salts, yellow precipitates of the *uranates*, $K_2U_2O_7$ and $Na_2U_2O_7$, are obtained. These are soluble in acids. In commerce the sodium salt is known as *uranium yellow*, and is employed for the yellow coloration of glass (uranium glass) and porcelain. The uranates can be obtained in crystalline form, by igniting uranyl chloride with alkali chlorides in the presence of ammonium chloride. Nascent hydrogen reduces uranic to uranous compounds.

The so-called *uranic-uranous oxide*, which constitutes uraninite, and is formed by the ignition of the other oxides in the air, must be viewed as uranous uranate, $2UO_3 . UO_2 = (\overset{VI}{U}O_2 . O_2)_2\overset{IV}{U}$.

Many uranium salts exhibit magnificent fluorescence. The oxide colors glass fluxes a beautiful greenish-yellow (uranium glass). Uranous oxide, UO_2, imparts a beautiful black color to glass and porcelain.

Besides these compounds, in which uranium appears to be quadrivalent and sexivalent, it also yields a **pentachloride**, UCl_5, like molybdenum and tungsten. The same results on conducting chlorine gas over a moderately heated mixture of carbon with one of the uranium oxides. It consists of dark needles which, in direct light, are metallic green, but in transmitted, ruby-red. It deliquesces in the air to a yellowish-green liquid; upon heating it is dissociated into uranous chloride and chlorine (at 120–235°).

There is also a *tetroxide*, UO_4, which, like the trioxide, UO_3, yields salts with the bases. It corresponds to molybdenum tetrasulphide MoS_4 (p. 383).

MANGANESE.

Mn = 55.0.

According to its atomic quantity, manganese bears the same relation to the elements of the chlorine group as chromium does to the elements of the sulphur group. The relationship manifests itself distinctly in the higher states of oxidation. Permanganic acid, $HMnO_4$, and its anhydride, Mn_2O_7, are perfectly analogous to perchloric, $HClO_4$, and periodic, HIO_4, acids and their anhydrides, Cl_2O_7 and I_2O_7. The permanganates and the perchlorates are very similar, and for the most part are isomorphous. The manganese in them appears to be septivalent, like the halogens in their highest state of oxidation. The similarity of manganese to the halogens is restricted to this one point of resemblance. In the rest of its derivatives, manganese shows great resemblance to the elements standing in the same horizontal series of the periodic system, viz., with chromium and iron (p. 393). Like these two elements, it forms compounds of the types:

$$MO\ (M(OH)_2 . MX_2), \qquad M_2O_3\ (M(OH)_3 . MX_3, \qquad MO_3\ (MO_4H_2).$$

1. In the manganous derivatives, MnX_2, the metal is bivalent. These salts are the more stable, and comprise the most common manganese compounds. They resemble and are usually isomorphous with the *ous* salts of iron and chromium, and the salts of metals of the magnesium group (p. 313).

2. The manganic compounds, MnX_3, are similar to and isomorphous with the ferric, chromic and aluminium derivatives; they are, however, less stable, and easily reduced to the manganous state.

3. The derivatives of manganic acid,

$$H_2MnO_4 = MnO_2(OH)_2,$$

in which manganese is sexivalent, are analogous to those of ferric (H_2FeO_4) and chromic acid (H_2CrO_4), and, of course, to those of sulphuric acid (H_2SO_4).

4. Manganese also yields derivatives which can be referred to the type M_2O_7. These are the *permanganates*, which correspond in formula to the persulphates. The manganese in them is apparently septivalent, but we have no definite knowledge of its structure, not even as to whether it corresponds to that of the persulphates (p. 297).

Consequently, in manganese we plainly observe how the similarity of the elements in their compounds is influenced by the valence (see p.

329). In the mangan*ous* condition, manganese, like the elements of the magnesium group, has a rather strong basic character, which diminishes considerably in the mangan*ic* state. Sexivalent manganese has a metalloidal acidic character, and, in manganic acid, approaches sulphur. By the further addition of oxygen, manganese finally (in permanganic acid) acquires a metalloidal character and resembles the halogens. We have already noticed that many other metals, especially chromium and iron, exhibit a similar behavior. Osmium in its tetroxide, OsO_4, wholly resembles the halogens.

On the other hand, the metalloidal and the weak basic metals acquire a strong basic, alkaline character, by the addition of hydrogen, or hydrocarbon groups (CH_3, C_2H_5). The univalent groups, NH_4 (ammonium), $P(CH_3)_4$ (tetramethyl phosphonium), $S(C_2H_5)_3$ (triethyl sulphine), $Sn(C_2H_5)_3$ (tin triethyl), etc., are of metallic nature, because their hydroxides, $P(CH_3)_4.OH$, $S(C_2H_5)_3.OH$, $Sn(C_2H_5)_3.OH$, are perfectly similar to the hydroxides (KOH, NaOH) of the alkali metals.

Manganese is widely distributed in nature. It is found native in meteorites. Its most important ores are pyrolusite, MnO_2, hausmannite, Mn_3O_4, braunite, Mn_2O_3, manganite, $Mn_2O_3.H_2O$, and rhodochrosite, $MnCO_3$.

Metallic manganese is obtained by igniting the oxides with aluminium powder (p. 347). It has a grayish-white color, is very hard, and fuses with difficulty (at about 1900°), and a little above this temperature it volatilizes. Its specific gravity is 7.2–8.0. It oxidizes readily in moist air. It decomposes water on boiling, and, when dissolved in acids, forms manganous salts.

The heat of formation of the most important manganese compounds corresponds to the symbols:

$$(Mn,O,H_2O) = 95 \qquad (Mn,Cl_2) = 112 \qquad (Mn,Cl_2,Aq) = 128$$
$$(Mn,O_2,H_2O) = 116 \qquad (Mn,S,O_4) = 245 \qquad (Mn,O_4,K) = 195.$$

MANGANOUS COMPOUNDS.

Manganous Oxide, MnO, results from ignition of the carbonate, with exclusion of air, and by heating all manganese oxides in hydrogen. It is a greenish, amorphous powder, which, in the air, readily oxidizes to manganous-manganic oxide, Mn_3O_4.

Manganous Hydroxide, $Mn(OH)_2$, is a voluminous, white precipitate, formed by the alkalies in manganous solutions. When exposed to the air, it oxidizes quickly to brown manganic hydroxide, $Mn_2(OH)_6$.

Manganous salts usually have a pale, reddish color, and are formed by the solution of manganese or oxides of manganese in acids.

Manganous Chloride, $MnCl_2$, crystallizes with four molecules of water in reddish tables. When heated, it decomposes into the oxide, hydrochloric acid and water. Anhydrous manganous chloride is prepared by igniting the double salt

$$MnCl_2 . 2NH_4Cl + H_2O$$

(see Magnesium Chloride), or by heating manganese oxides in hydrochloric acid gas; it is a crystalline, reddish mass, which deliquesces in the air.

Manganous Sulphate, $MnSO_4$, crystallizes below 6° with seven molecules of water (like magnesium and ferrous sulphates), at ordinary temperatures with $5H_2O$ (like copper sulphate); and above 25° with $4H_2O$; upon drying, the salt

$$MnSO_4 + H_2O$$

remains; the last molecule of water does not escape until at 280°. It forms double salts with the alkaline sulphates, *e. g.:*

$$MnSO_4 . K_2SO_4 + 6H_2O.$$

Manganous Carbonate, $MnCO_3$, exists in nature as rhodochrosite, and is precipitated by alkaline carbonates from manganous solutions, as a white powder, which turns brown on exposure to the air.

Manganous Sulphide, MnS, is found in nature as alabandite or manganese-blende. Alkaline sulphides precipitate a flesh colored sulphide from manganous solutions. It becomes brown in the air.

MANGANIC COMPOUNDS.

Manganic Oxide, Mn_2O_3, manganese sesquioxide, is a brown or black powder produced by the ignition of all the manganese oxides in a current of oxygen gas. It occurs as *braunite* in dark-brown quadratic crystals.

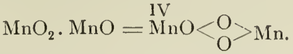
Manganic Hydroxide, $\overset{IV}{Mn_2}(OH)_6$ or $\overset{III}{Mn}(OH)_3$, manganic hydrate separates as a dark-brown precipitate on exposing ammoniacal solutions of manganous salts to the air. It dissolves in cold hydrochloric acid to a dark-brown liquid, containing, in all probability, *manganic chloride*, $MnCl_3$. When this is heated it decomposes into manganous chloride and chlorine.

Manganite, occurring in iron-black crystals, is the hydroxide, $\overset{IV}{Mn_2}O_2(OH)_2$ or $\overset{III}{Mn}O . OH$.

Manganous-manganic Oxide, $Mn_3O_4 = MnO . Mn_2O_3$. It constitutes the mineral *hausmannite*, crystallized in dark-gray quadratic octahedra, and is obtained as a reddish-brown powder by the ignition of all other manganese oxides in the air. It reacts with hydrochloric acid, according to the equation:

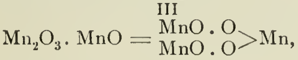
$$Mn_3O_4 + 8HCl = 3MnCl_2 + 4H_2O + Cl_2.$$

Since manganic oxide is quadratic in its crystallization, while all other sesquioxides (like corundum and hematite) are rhombohedral, and since the first is decomposed by dilute nitric and sulphuric acids into manganese dioxide, MnO_2, and a manganous salt, it has been generally supposed that manganic oxide is not a sesquioxide, but rather a compound of the dioxide with manganous oxide:



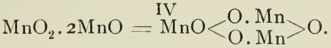
$$\mathrm{MnO_2 . MnO} = \overset{\mathrm{IV}}{\mathrm{Mn}}\mathrm{O}{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}{>}\mathrm{Mn}.$$

Hausmannite is quadratic, while other metallic oxides of the type M_3O_4 (the spinels, p. 351 and p. 377, and magnetite) are isometric; therefore the former is not considered a compound of manganese sesquioxide and protoxide:



$$\mathrm{Mn_2O_3 . MnO} = \begin{matrix}\overset{\mathrm{III}}{\mathrm{Mn}}\mathrm{O . O}\\ \mathrm{MnO . O}\end{matrix}{>}\mathrm{Mn},$$

but as manganous oxide and the dioxide:



$$\mathrm{MnO_2 . 2MnO} = \overset{\mathrm{IV}}{\mathrm{Mn}}\mathrm{O}{<}\begin{matrix}\mathrm{O . Mn}\\ \mathrm{O . Mn}\end{matrix}{>}\mathrm{O}.$$

This is shown by its behavior toward dilute nitric and sulphuric acids, which decompose it into manganese dioxide and two molecules of manganous oxide. Consult Franke, Jr. f. prakt. Ch. 36 (1887), 451. Chrysoberyl, unlike other spinels, is trimetric, and other reactions clearly prove (chiefly their deportment with concentrated sulphuric acid) that manganic and mangano-manganic oxides are to be regarded as sesquioxide derivatives.

Manganic oxide, like the other sesquioxides, is a very feeble base, which does not form salts with dilute or weak acids, and by separation of oxygen reverts to the manganous condition. Its salts are very unstable.

Manganic Sulphate, $Mn_2(SO_4)_3$, is obtained by the solution of manganic oxide, hydroxide, or, better, manganous-manganic oxide in concentrated sulphuric acid. When the last oxide is employed manganous sulphate also results. The best procedure is to heat the hydrate of manganese dioxide (see p. 390) with concentrated sulphuric acid to 168°, when the sulphate will separate as an amorphous, dark-green powder. It dissolves with a dark-red color in a little water. It is said to form *alums*, with potassium and ammonium sulphates, *e. g.*, $Mn_2(SO_4)_3 . K_2SO_4 + 24H_2O$, but Christensen's researches make this rather doubtful.

Manganese Dioxide, MnO_2, peroxide. This is the mineral pyrolusite, occurring in dark-gray radiating masses, or in almost black rhombic prisms, which possess metallic luster. When gently heated it is converted into oxide, by strong ignition into manganous-manganic oxide:

$$3MnO_2 = Mn_3O_4 + O_2.$$

It is used for making oxygen. Chlorine escapes when it is warmed with hydrochloric acid (p. 49):

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

The dioxide may be obtained artificially by heating manganous nitrate to 150–160°. Its *hydrates*, $MnO_2.H_2O$ and $MnO_2.2H_2O$, are produced on adding a hypochlorite to the solution of a manganous salt, or if chlorine be conducted through a solution of manganese containing sodium carbonate, or by adding potassium permanganate to a boiling solution of a manganous salt. The precipitated dioxide dissolves in cold hydrochloric acid, without liberating chlorine, as manganese tetrachloride, $MnCl_4$, is probably formed; when heat is applied it breaks down into manganous chloride, $MnCl_2$, and chlorine, Cl_2. This deportment would indicate that manganese is quadrivalent in the dioxide (p. 259). Manganese dioxide also unites with bases, yielding the so-called *manganites*, *e. g.*, $BaMn_2O_5$ and $K_2Mn_2O_5$.

Manganese peroxide (also Mn_2O_3 and Mn_3O_4) serves chiefly for the manufacture of chlorine gas, and it is, therefore, important from a technical point to estimate the quantity of chlorine which a given dioxide of manganese is able to set free. This is done by boiling the oxide with hydrochloric acid, conducting the liberated chlorine into a potassium iodide solution, and determining the separated equivalent amount of iodine by means of sodium hyposulphite. Or the oxide is heated in a flask with oxalic and sulphuric acids, when the oxalic acid is oxidized to carbon dioxide, and from the quantity of this set free we can calculate the quantity of active or available oxygen in the manganese oxide:

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2H_2O + 2CO_2.$$

In the preparation of chlorine the manganese is found in the residue as manganous chloride. With the relatively high value of pyrolusite, it is important for trade that the peroxide be recovered from the residue. This regeneration is at present largely executed by the method proposed by Weldon, according to which the manganous chloride, containing an excess of hydrochloric acid, is neutralized with lime, the clear liquid brought into a tall iron cylinder (the oxidizer), milk of lime added and air forced in. The mixture becomes warm, and so-called calcium manganite, $CaMnO_3 = CaO.MnO_2$, is precipitated as a black mud (Weldon's mud):

$$MnCl_2 + 2CaO + O = CaMnO_3 + CaCl_2.$$

The calcium chloride solution is run off, and the residual calcium manganite employed for the preparation of chlorine, when it conducts itself as a mixture of $MnO_2 + CaO$.

COMPOUNDS OF MANGANIC AND PERMANGANIC ACIDS.

When oxygen compounds of manganese are heated in the air in contact with potassium hydroxide, or, better, with oxidizing substances, like niter or potassium chlorate, a dark-green amorphous mass is produced, which dissolves in cold water with a dark-green color. When this solution is evaporated under the air-pump, dark-green, metallic, rhombic prisms of **potassium manganate**, K_2MnO_4, crystallize out. This salt is isomorphous with potassium sulphate and potassium chromate. It suffers no change by solution in potassium or sodium hydroxide, but is decomposed by water, brown hydrated manganese dioxide separating, and the green solution of the manganate changing into a dark-red solution of the permanganate, $KMnO_4$:

$$3K_2MnO_4 + 3H_2O = 2KMnO_4 + MnO_2.H_2O + 4KOH.$$

A similar conversion of the green manganate into red permanganate occurs more rapidly under the influence of acids or chlorine:

$$3K_2MnO_4 + 4HNO_3 = 2KMnO_4 + MnO_2 + 4KNO_3 + 2H_2O;$$
$$K_2MnO_4 + Cl = KMnO_4 + KCl.$$

The red solution again assumes a green color on the addition of a concentrated solution of an alkaline hydroxide.

Owing to this ready alteration in color the solution of the manganate is called *chameleon mineral.*

Potassium Permanganate, $KMnO_4$, is best prepared by conducting carbon dioxide into the manganate solution until the green color has passed into a red. Hydrated peroxide of manganese is precipitated. When the solution is concentrated the salt crystallizes in dark-red rhombic prisms isomorphous with potassium perchlorate, $KClO_4$. It is soluble in twelve parts of water at ordinary temperatures.

The permanganate solution is a strong oxidizing agent. If the oxidation takes place in the presence of a sufficient quantity of acid the permanganate is reduced to a faintly colored manganous salt:

$$2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 3H_2O + 5O.$$

When a permanganate solution is added to an acidulated ferrous solution, the former is decolorized, and there results a faintly yellow-colored solution of ferric and manganous salts:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O + K_2SO_4.$$

Hence the solution of this salt serves for the volumetric estimation of ferrous salts.

In *neutral* or *alkaline* solutions the permanganate in oxidizing is decomposed with the separation of manganese oxides:

$$2KMnO_4 + H_2O = 2MnO_2 + 2KOH + 3O.$$

In the same manner, the permanganate oxidizes and destroys many organic substances, therefore its solution cannot be filtered through paper without decomposition. It serves as a disinfectant.

The permanganate is also reduced by hydrogen peroxide in acid solution (p. 103).

The remaining permanganates are similar to and isomorphous with the perchlorates. The sodium salt is very soluble in water, and does not crystallize well.

Very cold sulphuric acid added to dry permanganate causes the separation of **Manganese Heptoxide,** Mn_2O_7, an oily, dark-colored liquid. By careful warming it is converted into dark-violet vapors, which explode when heated rapidly. Manganese heptoxide has a violent oxidizing action; paper, alcohol and other organic matter are inflamed by mere contact with it.

METALS OF GROUP VIII.

The last group of the periodic system comprises the elements:

Fe = 56 Ni = 58.7 Co = 59
Ru = 101.7 Rh = 103.0 Pd = 106
Os = 191 Ir = 193.0 Pt = 194.8.

These elements are the middle members of the three great periods, and they have no analogues in the two small periods (p. 245).

As regards both atomic weights and physical and chemical deportment, these elements constitute a transition from the preceding members of the great periods (Cr and Mn; Mo; W) to the next following members (Cu, Ag, Au, and Zn, Cd, Hg). The elements standing side by side (heterologous) and belonging to the same periods are very similar in their physical properties, and show, *e. g.*, very close specific gravities. They are, therefore, usually arranged in groups, and are distinguished as (1) the iron group (Fe, Ni, Co), with the specific gravity 7.8–8.6; (2) the group of the light platinum metals (Ru, Rh, Pd), with the specific gravity 11.8–12.1; and (3) the group of the heavy platinum metals (Os, Ir, Pt), with the specific gravity 21.1–22.4.

On the other hand, the homologous elements (Fe, Ru, Os; Ni, Rh, Ir; and Co, Pd, Pt) show a like similarity in their chemical properties, as do the other homologous elements. This resemblance shows itself chiefly in their combination forms, and, of course, too, in the properties of the compounds (p. 329). We know that the metals of group VI (chromium, molybdenum, tungsten) and of group VII (manganese) form the highest oxides (MeO_3 and Me_2O_7) having an acidic nature. In the adjacent elements of group VIII (iron, ruthenium, and osmium) we find salts:

$$K_2FeO_4, \quad K_2RuO_4, \quad K_2OsO_4,$$

derived from the unstable trioxides FeO_3, RuO_3 and OsO_3. This acid-forming function disappears in the following members, Ni, Rh, Ir, and Co, Pd, Pt; their chemical valences diminish rapidly and they attach themselves to Cu, Ag and Au.

Consequently the whole physical and chemical deportment of the nine elements about to be considered is governed by their position in the periodic system.

METALS OF THE IRON GROUP.

The metals of this group, iron, nickel and cobalt, are distinguished from all the other elements by their magnetic properties.

Iron forms three series of compounds after the forms, FeO_3, Fe_2O_3 and FeO. In its highest combinations iron has an *acidic* character, and the derivatives of ferric acid (H_2FeO_4) are perfectly similar to those of chromic and manganic acids; they are, however, less stable than the latter. Their analogues with cobalt and nickel are unknown.

The ferr*ic* compounds, FeX_3, are much like the aluminium, chromic and manganic derivatives. They are generally isomorphous with them. They are characterized among iron salts by their relative stability. The highest oxides of cobalt are far less stable, while the higher salts with nickel are unknown.

Again, iron, nickel and cobalt form *ous* compounds (FeX_2, NiX_2, CoX_2) in which they appear to be dyads. They resemble the compounds of chromium, manganese, and copper of the same form, and those of the magnesium metals. The ferrous salts are not as stable as the ferric; they are readily oxidized to the latter.

The cobaltous and nickelous compounds are quite stable, and in this respect these metals ally themselves with copper and zinc.

1. IRON.

$Fe = 56.0$.

This very important metal is widely distributed in nature. It is found native on the earth's surface almost exclusively in meteorites, which generally contain nickel. Iron granules free from the last metal are said to occur in the coal measures of Missouri. Iron is, however, present in great masses in other worlds which (like the sun) are surrounded by an atmosphere of glowing hydrogen, the heat of which is so intense that only the free elements can exist side by side (p. 29).

The most important iron ores are: magnetite (Fe_3O_4), hematite (Fe_2O_3), brown iron ore or limonite (hydrated oxide) and siderite ($FeCO_3$). These ores constitute almost the sole material for the manufacture of iron; the sulphide ores, like pyrite, are not so well adapted for iron making.

When iron is mentioned a distinction must be made between the metal iron, the pure element, and that iron which meets with a universal application in the arts and industries. The latter is really not a metal but an alloy of iron with carbon, and frequently also with silicon, phosphorus, sulphur, and manganese. Chemically pure iron, the real metal iron, is not applied technically because its production would be too expensive. Hence, a distinction must be made between chemically pure iron and the technical iron.

A. *Chemically pure iron.*

Chemically pure iron is obtained by heating the pure oxide or the oxalate in a current of hydrogen:

$$Fe_2O_3 + 3H_2 = 2Fe + 3H_2O;$$

to have complete reduction the temperature finally should reach 600°. If the reduction occurs at a red heat, the powder glows in the air, and burns (pyrophoric iron). The strongly ignited powder is not inflammable. Iron obtained by the electrolysis of ferrous sulphate always contains some hydrogen.

Chemically pure iron when hammered has a silver-white color, is tolerably soft, and is magnetizable. Its specific gravity is 7.78. It melts transitionally at 1800° and vaporizes at higher temperatures. In dry air it alters slowly but rusts rapidly in moist air. Boiling water is decomposed by finely divided pure iron with evolution of hydrogen. It dissolves readily in acids, and in nitric acid with the liberation of nitric oxide.

B. *Technical Iron.* This always contains carbon. The carbon content increases as the temperature, at which the ore is fused with the coal, rises. However, even at the most elevated temperatures iron does not take up more than 5 per cent. of carbon. The latter is either mechanically mixed as graphite with the iron or it exists as iron carbide, Fe_nC_m (*e. g.*, Fe_3C) chemically combined—alloyed.

The quantity of carbon and the form in which it exists leads to the varieties *cast iron*, *steel* and *wrought iron*, with their subdivisions.

I. **Cast Iron** contains 2.3 or more per cent. of carbon; its melting temperature rises as the carbon content falls (1050–1250°). It is brittle and cannot be welded or forged. The varieties of cast iron are:

(*a*) *White Iron.* All of its carbon is chemically combined. It is hard, brittle, and white in color. It is only made for conversion into wrought iron. White iron is distinguished as fibrous and "spiegeleisen," according to the appearance of its fracture.

(*b*) *Gray Iron.* Only a portion of its carbon is chemically combined with the iron. The greater portion exists as graphite. It is softer, more fusible than the preceding and of a bright gray to black color. It is used in the manufacture of castings, and of malleable iron; particularly by the Bessemer process.

In the production of the different kinds of iron not only carbon but also manganese and silicon play an important part. Their presence or absence also determines the nature of the iron. Manganese favors the chemical union of iron and carbon. Hence white iron is usually manganiferous. Silicon decomposes the alloy of iron and carbon and favors the production of graphite. The color of gray cast iron is determined by the size of the graphite plates. If they are very small the iron is fine-grained and its color light; otherwise the aggregation is coarsely crystalline and the color dark—light and dark gray, and black pig iron.

II. **Wrought Iron** and **Steel** with 1.6 per cent. and less of carbon. (Iron containing 1.6 to 2.3 per cent. of carbon is no longer manufactured technically.) It fuses with difficulty, but is malleable and can be welded. It melts at 1400° and higher. The method of preparation and the condition in which the malleable iron exists at the conclusion of its manufacture distinguish it as

A. Fluid Iron.
B. Weld Iron.

The first has been melted during its manufacture and is therefore free from slag, while the second variety has only been reduced to a pasty form and therefore contains slag. When a glowing piece of weld iron is suddenly cooled (*e. g.*, by immersion in water) its hardness is appreciably increased, in which case it is called *steel*, otherwise malleable or wrought iron. The following subdivisions are also known:

- A. Fluid Iron
  - tempered: Fluid steel.
  - not perceptibly tempered: Fluid weld iron.
- B. Weld Iron
  - tempered: Weld steel.
  - not perceptibly tempered: Wrought iron.

The hardening is generally influenced by the carbon content; steel contains from 0.6–1.6 per cent. and wrought iron less than 0.6 per cent. of carbon. However, the formerly customary distinction between steel and wrought iron on the basis of carbon content alone is no longer tenable, as at present tempered varieties of iron are produced, containing very considerable quantities of manganese, nickel, silicon, tungsten, and chromium, and very little carbon.

The classification just given of the technically available kinds of iron was prepared by an international commission at the Centennial Exposition in Philadelphia (1876), but it unfortunately has not been generally adopted.

Pig iron (crude iron) is always produced in blast furnaces by the reduction of its ores; while wrought iron is rarely made from ores directly, and never in blast furnaces. As a rule, wrought iron is manufactured from pig iron, as its name would imply.

Metallurgy of Iron.—The extraction of iron from its oxygen ores is based upon the reduction of the same by carbon at a red heat. In the oldest method, the ores were heated with carbon in forges; in this way the excess of air consumed the greater portion of the carbon, and the product was an iron poor in carbon, wrought iron, a spongy mass, which was then worked under the hammer. The present methods have been developed since the beginning of the fifteenth century. According to these pig iron is first prepared from the ores, and this afterwards converted into steel or wrought iron. The smelting of the ores is executed in large, walled blast furnaces, that permit the process to proceed without interruption. The furnaces are filled from openings above, with alternating layers of coal, broken ore and fluxes containing silica and lime; the fluxes facilitate the melting together of the reduced iron. The air necessary for the process is blown into the lower contracted portion of the furnace by means of a blowing engine. The combustion of the coal produces carbon monoxide, which reduces the iron oxides to metal:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

As the reduced iron sinks in the furnace it comes in contact with the coal, takes up carbon and forms cast iron, which fuses as it sinks lower and collects in the hearth of the furnace. Protracted and strong heating converts the chemically combined carbon into the graphitic form, and thus accelerates, with the assistance of silicon, the formation of the gray cast iron. The earthy impurities of the ores combine with the fluxes to a readily fusible *slag*, which envelops the fused iron and protects it from oxidation.

To convert the cast iron thus produced into wrought iron, carbon must be withdrawn from it. In making the wrought iron the cast iron is fused in open hearths (refining process), or in reverberatory furnaces with air access, and the mass stirred thoroughly until it has become pasty (puddling process). In this way almost all the carbon is burned to carbon monoxide and the other admixtures, like silicon, sulphur, and phosphorus, present in small quantities, are oxidized. The wrought iron is then worked up by rolling, or under the iron hammers (bar iron). If the decarburization be not carried quite as far the product will be steel (puddle steel). Such products are not free from slag. Cast iron can be changed into malleable iron by annealing. Castings of white iron are imbedded in ferric oxide powder and exposed for some time to a red heat. A portion of the carbon is lost and malleable iron results.

Steel can be manufactured from wrought-iron by cementation. The iron bars, mixed with fine charcoal, are exposed to a red heat, when the iron takes up carbon from the surface inward. The bars are then reforged, again heated with fine charcoal, and the process repeated until the mass becomes as homogeneous as possible (cementation steel). Cementation is just the opposite of annealing. A more homogeneous steel is obtained by refusion in crucibles (cast steel).

At present, steel is chiefly prepared directly from pig iron, by the method invented by Bessemer, in 1855. It consists in blowing air, under high pressure, into the molten iron, until the necessary amount of carbon has been burned out (Bessemer steel).

An iron rich in silicon (1.5–2 per cent. silicon) is well adapted for the purpose, because by the simultaneous combustion of the silicon the temperature is considerably increased. The operation is conducted in a pear-shaped vessel known as the converter. The air is blown in through openings in the bottom. The decarburization by the Swedish method only continues to the point where steel is fused. This is better accomplished by the English method, which removes the carbon so as to convert the mass into wrought iron, and then it is again carbonized by adding molten spiegeleisen, or by the addition of coke.

The Bessemer process originally was only adapted to crude iron containing as little sulphur and phosphorus as possible (at the highest, 0.05 per cent. phosphorus), because in this process the phosphorus is not consumed, but remains unaltered in the steel. By a slight, yet very essential alteration, Snelus (1872) and Thomas and Gilchrist (1878) rendered it suitable for iron containing much phosphorus. Their process is now known as the "basic process," and consists in lining the converter with a basic lining material of burnt dolomite. By contact with this substance the iron is completely dephosphorized and the phosphorus changed to calcium and magnesium phosphates.

The basic dephosphorizing method has attained very great importance because all the phosphorus contained in iron ores collects in the slag of the converter. The latter contains as much as 15–20 per cent. of phosphoric acid (and may even be increased to 24 per cent.), existing as calcium phosphate, and this may be applied as a fertilizer in agriculture (Thomas slag) (p. 305).

A third method (Siemens-Martin) of making steel consists in puddling the different varieties of iron together, or with iron ores. Siemens-Martin steel is obtained by fusing pig iron with wrought iron (old iron rails). It is much used. Uchatius steel is prepared by fusing granulated pig iron together with some iron ore and pyrolusite in graphite crucibles.

Ordinary iron, even the purest wire, always contains foreign ingredients, principally carbon and manganese, and minute quantities of silicon, sulphur, phosphorus, nitrogen, nickel, cobalt, titanium and other metals. The quantity of manganese is purposely increased (to 33 per cent.), as by this means the iron acquires valuable technical properties; it becomes more compact and solid. When iron, containing carbon, is dissolved in hydrochloric acid the chemically combined carbon unites with hydrogen, forming volatile hydrocarbons, while the mechanically admixed graphite remains behind. The total carbon is determined by the solution of the iron in bromine water or cupric chloride, when all the carbon remains behind.

Ordinary iron rusts rapidly in moist air, or it becomes covered with a layer of ferric hydroxide. When ignited in the air it is coated with a layer of ferrous-ferric oxide (Fe_3O_4) which is readily detached. It burns with an intense light in oxygen.

In contact with a magnet iron becomes magnetic; steel alone retains the magnetism, while cast iron and wrought iron soon lose this property after the removal of the magnet.

Iron decomposes water at a red heat, with the formation of ferrous-ferric oxide, and the liberation of hydrogen.

The metal dissolves readily in hydrochloric and sulphuric acids, with evolution of hydrogen; the latter has a peculiar odor, due to hydrocarbons which are liberated at the same time. Iron dissolves in nitric acid with evolution of nitrogen oxides. On dipping iron into concentrated nitric acid, and then washing it with water, it is no longer soluble in the acid (passive iron); this phenomenon is probably due to the production of ferrous oxide upon its surface.

FERROUS COMPOUNDS.

These are produced by the solution of iron in acids, and may also be obtained by the reduction of ferric salts:

$$Fe_2Cl_6 + Zn = 2FeCl_2 + ZnCl_2.$$

In the hydrous state they are usually of a green color; in the air they oxidize to ferric salts:

$$2FeO + O = Fe_2O_3.$$

Ferrous Chloride, $FeCl_2$, crystallizes from aqueous solutions in green monoclinic prisms, with four molecules of water. These deliquesce in the air and oxidize. Particularly beautiful crystals are obtained by exposing an alcoholic solution of ferric chloride in a closed vessel to the action of direct sunlight. The alcohol acts as a reducing agent and is oxidized to aldehyde (Organic Chemistry). The anhydrous salt is formed by conducting hydrogen chloride over heated iron. It is a white mass, which fuses on application of heat and sublimes at a red heat in white, six-sided leaflets. Its vapor density at 1300–1500° corresponds to the formula $FeCl_2$, but it appears that at lower temperatures it is also possible for the molecules Fe_2Cl_4 to exist.

It forms double salts with the alkaline chlorides, *e. g.*:

$$FeCl_2 . 2KCl + 2H_2O.$$

Ferrous Iodide, FeI_2, is obtained by warming iron with iodine and water. It crystallizes with four molecules of water.

Ferrous Oxide, FeO, is a black powder, resulting from the reduction of ferric oxide by carbon monoxide. When warmed in the air it oxidizes readily. **Ferrous Hydroxide**, $Fe(OH)_2$, is thrown out of ferrous solutions by the alkalies, as a greenish-white precipitate. Exposed to the air, it oxidizes, becoming reddish-brown. It is somewhat soluble in water, and has an alkaline reaction.

Ferrous Sulphate, $FeSO_4$, crystallizes with seven molecules of water in large, greenish, monoclinic prisms, and is generally called *green vitriol.* The crystals effloresce somewhat in dry air. They oxidize in moist air, and become coated with a brown layer of basic ferric sulphate. At 100° they lose six molecules of water, and change to a white powder. The last molecule of water escapes at 300°. Therefore, ferrous sulphate behaves just like the sulphates of the metals of the magnesium group (p. 315). Like them, it unites with alkaline sulphates to double sulphates, which contain six molecules of water, *e. g.*, $FeSO_4 . K_2SO_4 + 6H_2O$. These are more stable than ferrous sulphate, do not effloresce, and oxidize very slowly in the air.

The salt $FeSO_4 . (NH_4)_2SO_4 + 6H_2O$—*Mohr's salt*—is particularly characterized by its stability in the air, and is therefore employed to determine the strength of the potassium permanganate used in titrations.

Ferrous sulphate is obtained by dissolving iron in dilute sulphuric acid. Commercially, it may also be made from pyrite (FeS_2), which by careful roasting loses one atom of sulphur, and is converted into ferrous sulphide (FeS), which, in the presence of water, absorbs oxygen from the air, and is converted into sulphate, which may then be extracted by water.

Iron vitriol has an extended practical application; among other uses, it is employed in the preparation of ink, and in dyeing.

When heated it decomposes according to the following equation:

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2.$$

On this is based the production of fuming Nordhausen sulphuric acid (p. 194), and of colcothar.

Ferrous Carbonate, $FeCO_3$, exists in nature as siderite, crystallized in yellow-colored rhombohedra, isomorphous with calcite and smithsonite. Sodium carbonate added to ferrous solutions precipitates a white voluminous carbonate, which rapidly oxidizes in the air to ferric hydroxide. Ferrous carbonate is somewhat soluble in water containing carbon dioxide, hence present in many natural waters.

Ferrous Phosphate, $Fe_3(PO_4)_2 + 8H_2O$, occurs crystallized in bluish monoclinic prisms as *Vivianite*. Precipitated by sodium phosphate from ferrous solutions, it is a white amorphous powder, which oxidizes in the air.

Ferrous Sulphide, FeS, is a dark-gray, metallic mass, obtained by fusing together iron and sulphur. It is made use of in laboratories for the preparation of hydrogen sulphide. If an intimate mixture of iron filings and sulphur be moistened with water, the union will occur even at ordinary temperatures. Black ferrous sulphide is precipitated from ferrous solutions by alkaline sulphides. When the moist sulphide is exposed to the air it oxidizes to ferrous sulphate. The alkaline sulphides also precipitate ferrous sulphide from ferric salts, but the latter first suffer reduction:

$$2FeCl_3 + (NH_4)_2S = 2FeCl_2 + 2NH_4Cl + S,$$

and

$$FeCl_2 + (NH_4)_2S = FeS + 2NH_4Cl.$$

FERRIC COMPOUNDS.

Ferric Oxide, *Sesquioxide of iron*, Fe_2O_3, exists in nature, in compact, massive form, as red hematite, and as specular iron, in dark-gray metallic rhombohedra. It may be prepared by heating the iron oxygen compounds in the air, and is obtained on a large scale by the ignition of green vitriol. It is then a dark-red powder (*colcothar* or *caput mortuum*) used as a paint and for polishing glass.

Ferric Hydroxide, $Fe(OH)_3$, is precipitated by alkalies from ferric solutions as a voluminous, reddish-brown mass. On boiling, it becomes more compact, gives up water, and is converted into the hydrate, $Fe_2O(OH)_4$. Many iron ores, like xanthosiderite, $Fe_2O(OH)_4$, göthite, $Fe_2O_2(OH)_2$ (isomorphous with diaspore, p. 350), and limonite, $Fe_4O_3(OH)_6$, are analogous compounds.

Freshly precipitated ferric hydroxide is soluble in a solution of ferric chloride or acetate. When such a solution is subjected to dialysis, the iron salt diffuses, and there remains a pure aqueous solution of ferric hydroxide. All of the latter is precipitated as a jelly from such a solution upon the addition of a little alkali or acid.

Ferrous-ferric Oxide, $Fe_3O_4 = FeO.Fe_2O_3$, occurs in nature crystallized in black regular octahedra—magnetite. It is abundant in Sweden and Norway, and in the Urals. It may be obtained artificially by conducting steam over ignited iron (p. 397). Magnetite constitutes the natural loadstone.

Ferric hydroxide, like other sesquioxides, is a feeble base, and does not yield salts with weak acids, like carbonic or sulphurous (p. 269).

Ferric salts arise by the solution of ferric oxide in acids, or by the oxidation of ferrous salts in the presence of free acids (best by chloric or nitric acids):

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

Most of the ferric salts have a yellow-brown color, and are converted by reduction into ferrous salts:

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

Ferric Chloride, $FeCl_3$. It is obtained in aqueous solution by conducting chlorine into a solution of ferrous chloride:

$$2FeCl_2 + Cl_2 = 2FeCl_3.$$

The hydrate, $2FeCl_3 + 3H_2O$, remains upon evaporation. It is a yellow crystalline mass, readily soluble in water, alcohol, and ether. When heated, it is partly decomposed, hydrogen escapes, and a mixture of chloride and oxide remains.

Anhydrous ferric chloride is produced by heating iron in a current of chlorine gas; it sublimes in brownish-green, metallic, shining, six-sided prisms and scales, which deliquesce in the air. Ferric chloride boils at 280–285°. Its vapor density between 320–440° closely approximates the formula Fe_2Cl_6; with rising temperature it diminishes gradually, and from 750–1050° corresponds to the simple formula $FeCl_3$. The vapor, however, probably does not consist of these molecules, because at 440° a decomposition into ferrous chloride, $FeCl_2$, and chlorine commences (Friedel and Crafts, Ber. (1888) **21**, Ref. 580). Recently the molecular formula $FeCl_3$ has been found by determining the rise in the boiling point of ethereal and alcoholic solutions of ferric chloride.

Ferric chloride solutions can take up large quantities of ferric hydrate. In the resulting, dark-colored solutions ferric hydroxychlorides are present:

$$nFeCl_3 + mFe_2O_3 + xH_2O \text{ (\textit{Liquor ferri oxychlorati})}.$$

Ferric Sulphate, $Fe_2(SO_4)_3$, is obtained by dissolving the oxide in sulphuric acid. When its solution is evaporated, it remains as a white mass, which gradually dissolves in water, with a reddish-brown color. It forms alums (p. 352) with alkaline sulphates, *e. g.*:

$$\underset{\text{Potassium iron alum.}}{Fe_2(SO_4)_3.K_2SO_4 + 24H_2O.}$$

Ferric Phosphate, $FePO_4$, is a yellowish-white precipitate, thrown out of ferric solutions by sodium phosphate. It is insoluble in water and acetic acid.

Iron Disulphide, FeS_2, occurs in nature as iron *pyrites*, crystallized in yellow, metallic, shining, octahedra or pentagonal dodecahedra. It is employed in the manufacture of sulphuric acid and green vitriol. The artificial sulphide can be prepared in many ways. It leaves ferrous sulphide when it is strongly heated in hydrogen.

COMPOUNDS OF FERRIC ACID.

On fusing iron filings with niter, or by conducting chlorine into potassium hydroxide, in which ferric hydroxide is suspended, *potassium ferrate*, K_2FeO_4, is produced, and crystallizes from the alkaline solution in dark-red prisms. This salt is isomorphous with potassium chromate and sulphate. It dissolves quite easily in water; but the dark-red liquid soon decomposes with separation of ferric hydroxide and evolution of oxygen. The free acid is not known, as it immediately breaks down when liberated from its salts.

CYANOGEN DERIVATIVES OF IRON.

When potassium cyanide is added to aqueous solutions of the ferrous or ferric salts, the cyanides, $Fe(CN)_2$ and $Fe(CN)_3$, are thrown down as yellowish precipitates, which decompose rapidly in the air. They dissolve in an excess of potassium cyanide to form the double cyanides, $Fe(CN)_2.4KCN$ and $Fe(CN)_3.3KCN$. When acids are added to strong solutions of these salts the hydrogen compounds, $H_4Fe(CN)_6$, and $H_3Fe(CN)_6$ separate. Like the halogen hydrides they are acids and form salts by exchanging their hydrogen for metals. The iron and the cyanogen group in these salts and in the free acids cannot be detected by the usual reagents (*e. g.*, the iron is not precipitated by the alkalies). It is supposed that compound groups of peculiar structure are present in these double cyanides, and that they conduct themselves like the halogens. The group, $FeCy_6$, in the ferr*ous* compounds is called *ferrocyanogen*, that of $FeCy_6$ in the ferr*ic*, *ferricyanogen*. (Nothing is known in regard to the molecular magnitude of these compounds; $Cy = CN$). The ferro- behave toward the ferri-compounds the same as the ferrous toward the ferric salts; oxidizing agents convert the former into the latter, and reducing agents transform the latter into the former:

$$K_4Fe(CN)_6 + Cl = K_3Fe(CN)_6 + KCl$$

and

$$K_3Fe(CN)_6 + KOH + H = K_4Fe(CN)_6 + H_2O.$$

Cobalt, manganese, chromium and the platinum metals afford similar cyanides (pp. 377, 407).

Metallic acid radicals such as are known to exist in the chromates, manganates, permanganates and ferrates are assumed to be present in the ferro- and ferricyanides. Such radicals, with a basic character, have been encountered: the radicals $(W_3Cl_4)^{II}$ and $(Mo_3Cl_4)^{II}$ which play the rôle of a bivalent metal towards the halogens in the compounds—chlor-tungsten hydroxide and chlor-molybdenum hydroxide (p. 382).

All of these radicals have this in common—the metal present in the radical is no longer detected by the reagents to which it responds when existing as metal in its salts. This it will only do after the radical has been destroyed. If the radicals contain halogens they too will behave like the metals. This failure to respond to the usual reagents is an indication that the metal or halogen belongs to a compound radical and does not act as an independent part in the molecule. As mentioned on p. 270, salts, bases and acids are regarded as compounds of two members when they are resolved in aqueous solution into two kinds of ions. Numerous transpositions and particularly those of analytical value occur between ions, hence they are briefly termed "ion reactions." Every ion, be it simple or compound, is characterized by reactions which belong to it alone and by which it is detected. Hence in general we cannot speak of the reactions of the elements, *e. g.*, of iron, when search is being made for its presence, but we must rather consider the condition, the combination form, the nature of the ion, for which the reaction has value. There are no general reagents or reactions for iron, but only those for metallic iron, or for ferrous, ferric, and ferrocyanide compounds, etc.; no general reaction for chlorine, but only such as answer for free chlorine, hydrogen chloride, chloric acid, perchloric acid, etc.—reactions of the ions according to the theory of electrolytic dissociation. This is expressed in the following formulas which are divided by lines into their ions:

$$\mathrm{Fe}\,|\,\mathrm{Cl_2} \qquad \mathrm{K_4}\,|\,(\mathrm{FeCy_6}) \qquad \mathrm{H}\,|\,\mathrm{Cl} \qquad \mathrm{H}\,|\,(\mathrm{ClO_3}) \qquad \mathrm{Mn}\,|\,(\mathrm{SO_4}) \qquad \mathrm{K_2}\,|\,(\mathrm{MnO_4})$$
$$\mathrm{Mo}\,|\,\mathrm{Cl_4} \qquad (\mathrm{Mo_3Cl_4})\,|\,\mathrm{Cl_2} \qquad \mathrm{Cr_2}\,|\,(\mathrm{SO_4})_3 \qquad \mathrm{K_2}\,|\,(\mathrm{CrO_4}).$$

Potassium Ferrocyanide, *Yellow prussiate of potash,* $K_4Fe(CN)_6$, is produced by the action of potassium cyanide upon iron compounds, or upon free iron (in which case the oxygen of the air or water takes part). It is prepared commercially by igniting carbonized nitrogenous animal matter (blood, horns, hoofs, leather offal, etc.) with potashes and iron.

In this operation, the carbon and nitrogen of the organic matter combine with the potassium of the potashes to form potassium cyanide, while the sulphur present forms iron sulphide with the iron. (By means of alcohol, potassium cyanide can be extracted from the fusion.) Upon treating the fusion with water, the potassium cyanide and iron sulphide react upon one another, and potassium ferrocyanide results and is purified by crystallization:

$$\mathrm{FeS + 6KCN = K_4Fe(CN)_6 + K_2S.}$$

In Germany, at present, yellow prussiate of potash is manufactured exclusively from the material used in purifying gas (p. 105), which contains the greater part of the cyanogen of the crude gas in the form of Prussian blue and ammonium sulphocyanide. The first is transformed by lime into ferric oxide and calcium ferrocyanide, which in aqueous solution is changed by potassium chloride to calcium chloride and very sparingly soluble potassium calcium ferrocyanide:

$$\mathrm{Ca_2Fe(CN)_6 + 2KCl = CaK_2Fe(CN)_6 + CaCl_2.}$$

Potashes are finally used to convert the insoluble salt into calcium carbonate and potassium ferrocyanide.

It crystallizes from water in large, yellow, monoclinic prisms, having three molecules of water, and soluble in 3–4 parts of water. The crystals lose all their water at 100°, and are converted into a white powder. At a red heat the ferrocyanide breaks down into potassium cyanide, nitrogen, and iron carbide (FeC_2). When the salt is warmed with dilute sulphuric acid, half of the cyanogen escapes as hydrogen cyanide; concentrated sulphuric acid decomposes it, according to the following equation:

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = FeSO_4 + 2K_2SO_4 + 3(NH_4)_2SO_4 + 6CO.$$

When strong hydrochloric acid is added to a concentrated solution of potassium ferrocyanide *hydrogen ferrocyanide*, H_4FeCy_6, separates as a white crystalline powder, which soon turns blue in the air. It is an acid. Its salts with the alkali and alkaline earth metals are very soluble in water. The sodium salt crystallizes with difficulty. The salts of the heavy metals are insoluble in water, and are obtained by double decomposition. When potassium ferrocyanide is added to the solution of a ferric salt a dark-blue cyanide

$$Fe_7(Cy)_{18} = (Fe_2)_2(FeCy_6)_3,$$

called *Prussian blue*, is precipitated:

$$3K_4FeCy_6 + 4Fe_2Cl_6 = (Fe_2)_2(FeCy_6)_3 + 12KCl.$$

This color was discovered accidentally by Diesbach, of Berlin, in 1704. It is the ferric salt of hydroferrocyanic acid; and if potassium or sodium hydroxide is poured over it, it is converted into ferrocyanide of potassium and ferric hydroxide:

$$\overset{VI}{(Fe_2)_2}(FeCy_6)_3 + 12KOH = 3K_4FeCy_6 + 4\overset{VI}{Fe}(OH)_3.$$

Potassium ferrocyanide produces a reddish-brown precipitate of copper ferrocyanide, Cu_2FeCy_6, in copper solutions; and in ferrous solutions a white precipitate, which on exposure to the air rapidly becomes blue in color.

Oxidizing agents convert the ferro- into **potassium ferricyanide,** K_3FeCy_6, *red prussiate of potash.* This conversion is most conveniently effected by conducting chlorine into the solution of the yellow prussiate:

$$2K_4FeCy_6 + Cl_2 = 2K_3FeCy_6 + 2KCl.$$

The quadrivalent ferrocyanogen group, $FeCy_6$, is then changed to the trivalent ferricyanogen group, $FeCy_6$ (p. 401). $Cy = CN$.

The red prussiate crystallizes from water in red rhombic prisms. The free hydroferricyanic acid, $H_3Fe(CN)_6$, is precipitated upon the addition of concentrated hydrochloric acid. It is rather unstable.

With ferrous solutions potassium ferricyanide yields a dark-blue precipitate, $Fe_5Cy_{12} = Fe_3Fe_2Cy_{12}$, very similar to Prussian blue, and called *Turnbull's blue:*

$$2K_3FeCy_6 + 3FeSO_4 = Fe_5Cy_{12} + 3K_2SO_4.$$

So far as its formation is concerned, Turnbull's blue is the ferrous salt of hydroferricyanic acid, $[\overset{III}{Fe}(CN)_6]\overset{II}{Fe}_3$. Although hot alkalies decompose it into potassium ferrocyanide and ferrous-ferric hydroxide, this is most probably due to the fact that the potassium ferricyanide and ferrous hydroxide, which are produced at first, are transposed by the alkali into potassium ferrocyanide and ferrous-ferric hydrate :

$$2Fe(CN)_6K_3 + 2KOH + 3Fe(OH)_2 = 2K_4Fe(CN)_6 + 2Fe(OH)_3 + Fe(OH)_2.$$

Very probably in the precipitation potassium ferricyanide and the ferrous salt transpose into potassium ferrocyanide and a ferrous-ferric salt ; then Turnbull's blue would have to be regarded as the ferric-ferrous salt of hydroferrocyanic acid—$\overset{III}{Fe_2}\overset{II}{Fe}[\overset{IV}{Fe(CN)_6}]_2$. Turnbull's blue is the principal constituent of commercial Prussian blue, which also contains, because of its preparation from impure materials, ferriferrocyanide, $Fe_7(CN)_{18}$. The latter largely comprises Parisian blue.

Potassium ferricyanide does not cause precipitation in ferric solutions. By these reactions, ferric salts may be readily distinguished from the ferrous. Potassium sulphocyanide (KCNS) produces a dark-red coloration in ferric solutions, while it leaves the ferrous unaltered.

Iron, like nickel (p. 233), combines with carbon monoxide to a volatile, gaseous body—**Iron Carbonyl** [Mond and Quincke, Ber. (1891) **24**, 2248 ; Berthelot, Compt. rend. (1891) **112**, 1343], which, from its composition, is probably **Iron Tetracarbonyl**, $Fe(CO)_4$. This substance is produced by conducting carbon monoxide over very finely divided iron at 40–80°, or under a pressure of eight atmospheres [Roscoe and Scudder, Ber. (1891) **24**, 3843]. It is decomposed with the formation of an iron mirror when it is passed through a glass tube heated to 200–350°.

Iron pentacarbonyl, $Fe(CO)_5$, and *heptacarbonyl*, $Fe_2(CO)_7$, have been prepared. The first is a yellow liquid, boiling at 103°, from which the second separates, on exposure to the light, in golden crystals. Carbon monoxide is evolved at the same time.

2. NICKEL.

Ni = 58.7.[*]

Nickel exists in native condition in meteorites; its most important ores are niccolite, NiAs, and gersdorffite, $NiS_2 . NiAs_2$ (constituted like cobaltite). The arsenical ores are now of little importance in the nickel industry. The chief sources of the metal are at present nickeliferous phyrrotite and the nickel silicates (Canada, Norway and New Caledonia). Garnierite—a New Caledonian mineral—a silicate, containing also iron, calcium and magnesium, may be especially noticed in this connection. Nickel is almost always accompanied in its ores by cobalt, and *vice versâ*, cobalt usually by nickel. The isolation of the latter from its ores and from speiss-cobalt (p. 406) is very complicated. Nickel usually appears in commerce in cubical forms, which in addition to the chief ingredient always contain some copper, bismuth, and other metals. Chemically pure nickel is procured by igniting the oxalate in a current of hydrogen. Nickel is almost silver-white in color and is very lustrous, and very

---

[*] See Th. W. Richards and A. S. Cushman, Z. f. anorg. Chem. 20 (1899), 352.

tenacious. Its specific gravity varies from 8.8 to 9.1. It fuses at a somewhat lower temperature than iron, and like it is attracted by the magnet. It is not altered in the air; it dissolves with difficulty in hydrochloric and sulphuric acids, but readily in nitric acid.

Its derivatives are almost exclusively of the *ous* form, NiX_2; nickelic oxide behaves like a peroxide, and does not form corresponding salts.

Nickelous Hydroxide, $Ni(OH)_2$, is a bright green precipitate produced by alkalies in nickelous solutions. It dissolves in ammonium hydroxide, with a blue color. When heated it passes into gray nickelous oxide, NiO.

Nickelous Chloride, $NiCl_2 + 6H_2O$, consists of green, monoclinic prisms. When heated they lose water and become yellow.

Nickelous Cyanide, $Ni(CN)_2$, is precipitated by potassium cyanide as a green-colored mass from nickel solutions. It is soluble in excess of the precipitant. The double cyanide, $NiCy_2.2KCy + H_2O$, crystallizes from the solution. This salt is readily decomposed by acids. Cyanogen compounds of nickel, constituted like those of iron and cobalt, are not known.

Nickelous Sulphate, $NiSO_4 + 7H_2O$, appears in green, rhombic prisms, isomorphous with the sulphates of the magnesium group, and forms analogous double salts.

Nickelous Sulphide, NiS, is precipitated, black in color, by alkaline sulphides from nickel solutions.

Nickelic Oxide, Ni_2O_3 and **Hydroxide,** $Ni_2(OH)_6$, are perfectly similar to the corresponding cobalt salts; when warmed with hydrochloric acid they liberate chlorine.

Nickel Tetracarbonyl, $Ni(CO)_4$, see pp. 234, 404.

Nickel is used for certain alloys *Argentan* consists, ordinarily, of 50 per cent. of copper, 25 per cent. of nickel and 25 per cent. of zinc. The white color, the hardness and the power of receiving a higher polish increase with the increase in the nickel content. The iron-nickel alloys have great technical importance (nickel steel). The German nickel coins in which we have evidence of the great coloring power of nickel consist of 75 per cent. of copper and 25 per cent. of nickel. Nickel alloys are used to make electrical resistances; their conductivity is slight and little depends on this at the ordinary temperature (*manganin:* 84 per cent. of copper, 4 per cent. of nickel, 12 per cent. of manganese; *constantan:* 60 per cent. of copper, 40 per cent. of nickel, etc.). At present, cast-iron ware is coated with a layer of nickel to prevent it from rusting and to impart to it a beautiful white surface. This is accomplished by electroplating, or by boiling the iron ware in a solution of zinc chloride and nickel sulphate.

In the electrolytic method a solution of the double sulphate of nickel and ammonium is employed; the positive electrode consists of a pure nickel plate, while the object to be coated forms the negative electrode.

3. COBALT.

$Co = 59$.*

Cobalt occurs in nature as smaltite ($CoAs_2$) and cobaltite ($CoAs_2 . CoS_2$). The metal is obtained by the ignition of cobaltous oxide with carbon, or in a current of hydrogen. It has a reddish-white color and strong luster, is very tenacious, and fuses with difficulty. Its specific gravity is 8.5. It is attracted by magnets, but to a less degree than iron. It is not altered by the air or water. It is only slightly attacked by hydrochloric and sulphuric acids; nitric acid dissolves it readily, forming cobaltous nitrate.

The predominating compounds have the form CoX_2, and are called *cobaltous*. They are very stable, and generally isomorphous with the corresponding ferrous salts. The hydrous cobaltous compounds have a reddish color, the anhydrous are blue.

COBALTOUS COMPOUNDS.

Cobaltous Chloride, $CoCl_2$, is obtained by the solution of cobaltous oxide in hydrochloric acid, and crystallizes with six molecules of water in red monoclinic prisms. When heated, it loses water, and becomes anhydrous and blue in color. Characters made with this solution upon paper are almost invisible, but when warmed they become distinct and blue (sympathetic ink).

Cobaltous Hydroxide, $Co(OH)_2$, is a reddish precipitate produced by the alkalies in hot, cobaltous solutions. When exposed to the air, it is colored brown by oxidation. Basic salts are precipitated from cold solutions; these dissolve with a blue color in an excess of concentrated alkalies. When heated out of air contact, the hydroxide passes into green *cobaltous oxide*, CoO.

Cobaltous Sulphate, $CoSO_4 + 7H_2O$, crystallizes in dark-red monoclinic prisms; the hydrated sulphate, $CoSO_4 + 6H_2O$, separates from hot solutions. It is isomorphous with ferrous sulphate, and yields double salts with alkaline sulphates (p. 398).

Cobaltous Nitrate, $Co(NO_3)_2 + 6H_2O$, forms red deliquescent prisms.

Cobaltous Sulphide, CoS, is a black precipitate, produced in neutral cobalt solutions by alkaline sulphides. It is insoluble in dilute acids.

Cobalt Silicates.—When glass is fused with a cobalt compound it is colored a dark blue, and when reduced to a powder is used as a pigment under the name of *smalt*.

Smalt is prepared commercially by fusing cobalt ores with potashes and quartz. The cobalt forms a silicate (smalt) with the silica and potassium, while the other metals, such as bismuth, arsenic, and especially nickel, accompanying it in its ores, are thrown out as a metallic mass. This is called speiss-cobalt and serves for the preparation of nickel.

---

* See Cl. Winkler, Z. f. anorg. Ch. 17 (1898), 236.

On igniting cobalt oxide, Co_2O_3, with alumina, a dark-blue mass is produced—*cobalt ultramarine* or *Thénard's blue*. When zinc oxide and cobalt oxide are ignited a green color—*green cinnabar* or *Rinmann's green*—is obtained.

COBALTIC COMPOUNDS.

Cobaltic Oxide, Co_2O_3, is left as a black powder on the ignition of cobaltous nitrate. It becomes cobaltous-cobaltic oxide, Co_3O_4, at a red heat, and cobaltous oxide at a white heat. The hydroxide, $Co_2(OH)_6$, separates as a dark-brown powder, if chlorine be passed through an alkaline solution containing a cobaltous salt.

A cobaltous salt is produced and oxygen set free, when sulphuric acid acts upon the oxide or the hydroxide. Chlorine is generated when it is heated with hydrochloric acid:

$$Co_2O_3 + 6HCl = 2CoCl_2 + 3H_2O + Cl_2.$$

The cobaltic hydroxide dissolves in dilute, cold hydrochloric acid, with scarcely any liberation of chlorine; the solution probably contains cobaltic chloride, $CoCl_3$, which decomposes into cobaltous chloride and chlorine on evaporation.

Cobaltous-cobaltic Oxide, $Co_3O_4 = Co_2O_3 . CoO$, corresponding to magnetite, Fe_3O_4, is formed upon the ignition of the oxygen cobalt derivatives in the air, and is a black powder.

It is noteworthy that cobalt is capable of yielding complex derivatives in which it appears to be in union with the groups NO_2, CN or NH_3, forming peculiar radicals. One of the most interesting of these is **potassium cobaltic nitrite** (Fischer's salt).

When potassium nitrite, KNO_2, is added to a cobaltous solution acidified with acetic acid, nitric oxide is set free, and in course of time

$$Co(NO_2)_3 . 3KNO_2 + nH_2O,$$

a double salt, separates as a yellow crystalline powder. This should be viewed as the potassium salt of a hydronitroso-cobaltic acid:

$$H_3Co(NO_2)_6.$$

This reaction is very characteristic for cobalt, and serves to separate it from nickel.

Ammonia-cobalt Compounds.—Numerous cobaltamines are known. On adding ammonium hydroxide to a cobaltous chloride solution, the precipitate first formed dissolves in the excess of the reagent, and when this liquid is permitted to stand exposed to the air, the color, which is brown at first, gradually passes into red. On adding concentrated hydrochloric acid to this solution, a brick-red, crystalline powder, of the composition

$$Co_2Cl_6 . 10NH_3 + 2H_2O,$$

called *roseocobaltic chloride*, is precipitated. If, however, the red solution be boiled with hydrochloric acid, a red powder, *purpureocobaltic chloride*,

$$Co_2Cl_6.10NH_3,$$

separates out. If the ammoniacal red solution contain much ammonium chloride, hydrochloric acid will precipitate a yellowish-brown compound—*luteocobaltic chloride*,

$$Co_2Cl_6.12NH_3.$$

These derivatives are supposed to contain compound basic radicals in which cobalt, halogens and ammonia are all present.

The other salts of cobalt, such as the sulphate and nitrate, yield similar compounds, *e. g.*

$$Co_2(NO_3)_6.10NH_3,$$

roseocobaltic nitrate.

Cyanogen Cobalt Compounds.—In solutions of cobaltous salts, potassium cyanide produces a bright brown precipitate of *cobaltocyanide*,

$$Co(CN)_2,$$

soluble in an excess of the reagent. The solution absorbs oxygen from the air, and is converted into *potassium cobalticyanide*,

$$K_3Co(CN)_6,$$

corresponding to potassium ferricyanide. When the solution is evaporated the cobalticyanide crystallizes in colorless rhombic prisms, very soluble in water. Sulphuric acid precipitates *hydrogen cobalticyanide*,

$$H_3Co(CN)_6,$$

from the concentrated solution. This acid crystallizes in needles.

GROUP OF THE PLATINUM METALS.

Besides platinum, this group comprises palladium, rhodium, ruthenium, osmium, and iridium—the constant companions of the first in its ores. On p. 392 we observed that these metals are divided into two groups: the *group of light platinum metals*, and the *group of heavy platinum metals*. The latter have higher atomic weights and specific gravities:

	Ru, 101.7	Rh, 103.0	Pd, 106	Os, 191	Ir, 193.0	Pt, 194.8
Sp. gr.	“ 12.3	“ 12.1	“ 11.5	“ 22.48	“ 22.4	“ 21.5
At. vol.	“ 8.3	“ 8.6	“ 9.1	“ 8.4	“ 8.6	“ 9.0.

The relations of the metals of these two groups to each other are perfectly similar to those of the iron group. Osmium and ruthenium, like iron, have a gray color, fuse with difficulty, and are readily oxidized in the air. Palladium and platinum, on the other hand, have an almost silver-white color like nickel, are more easily fusible, and are not oxidized by oxygen. In chemical respects osmium and ruthenium, like iron, also show a metalloidal nature, inasmuch as their highest oxygen compounds form acids. Their derivatives show a complete parallelism with those of iron:

II	III	IV	VI
OsO	Os_2O_3	OsO_2	(OsO_3)
Osmous oxide.	Osmic oxide.	Osmium dioxide.	Osmium trioxide.
RuO	Ru_2O_3	RuO_2	(RuO_3)
Ruthenious oxide.	Ruthenic oxide.	Ruthenium dioxide.	Ruthenium trioxide.

The acid oxides OsO_3 and RuO_3 are unknown, but the corresponding acids, H_2OsO_4 (osmic acid) and H_2RuO_4 (ruthenic acid), and their salts have been obtained. Besides the derivatives already mentioned we find that osmium and ruthenium are capable of still higher oxidation, yielding OsO_4, per-osmic anhydride, and RuO_4, per-ruthenic anhydride—which is not the case with iron; in these compounds the metals appear to be octads, yet these oxides do not form corresponding acids or salts.

Rhodium and iridium, like cobalt, do not yield acid-like derivatives. Their salts correspond to the forms:

II	III	IV
RhO	Rh_2O_3	RhO_2
Rhodous oxide.	Rhodic oxide.	Rhodium dioxide.

The rhodic compounds are the more stable derivatives.

Palladium and platinum, finally, are relatively of more basic nature, as their *ous* derivatives, PdX_2 and PtX_2, are proportionally more stable than the *ic* forms, PdX_4 and PtX_4. Palladium also forms a lower oxide, palladium suboxide, Pd_2O, in which it approaches silver.

The platinum metals are found in nature almost exclusively in the so-called platinum ore, which usually occurs in small metallic grains in accumulated sands of a few regions (in California, Australia, the island of Sumatra, and especially in the Urals). The platinum ore, like that of gold, is obtained by the elutriation of the platiniferous sand with water, whereby the lighter particles are carried away. Platinum ore usually contains 50–80 per cent. of platinum, besides palladium (to 2 per cent.), iridium (to 7 per cent.), osmium (1½ per cent.), and ruthenium (1½ per cent.), and different other metals, as gold, copper, and iron.

The *separation of the platinum metals* is generally executed in the following manner: The gold is first removed by dilute aqua regia. Then the ore is treated with concentrated aqua regia, when platinum, palladium, rhodium, ruthenium, and a portion of iridium are dissolved. Metallic grains or leaflets, an alloy of osmium and iridium—platinum residues—remain. Ammonium chloride is then added to the solution and platinum and iridium precipitated as double salts. When the precipitate is ignited, a spongy mass of iridium-bearing platinum (platinum sponge) is obtained, which is applied directly in the manufacture of platinum vessels. The filtered solution from the insoluble chlorides contains palladium, rhodium, and ruthenium, which are thrown down as a metallic powder by iron; their further separation is then effected in various ways.

Formerly spongy platinum was employed almost exclusively for the manufacture of platinum objects; it was pressed into moulds, then ignited and hammered out. Now the fusibility of platinum in the oxyhydrogen flame is resorted to, and the fused metal run into moulds.

Platinum containing both iridium and rhodium may be fused directly out of the platinum ore by means of the oxyhydrogen blowpipe. The greater portion of the osmium and ruthenium is consumed in this operation. The presence of iridium and rhodium makes platinum harder and less readily attacked by many reagents.

RUTHENIUM AND OSMIUM.

Ru = 101.7. Os = 191.

Ruthenium, discovered by Claus in 1845, has a steel-gray color; it is very hard, brittle, and difficultly fusible (at about 1800°). When pulverized and ignited in the air it oxidizes to RuO, Ru_2O_3 and RuO_2. It is insoluble in acids, and only slowly dissolved by aqua regia. When fused with potassium hydroxide and nitrate, it forms potassium ruthenate, K_2RuO_4.

Ruthenium heated in chlorine gas yields *ruthenium dichloride*, $RuCl_2$, a black powder, insoluble in acids. The *trichloride*, $RuCl_3$, is obtained by the solution of $Ru_2(OH)_6$ in hydrochloric acid, and is a yellow, crystalline mass, which deliquesces in the air. It yields crystalline double chlorides with potassium and ammonium chlorides, *e. g.*, $RuCl_3.KCl$. The *tetrachloride*, $RuCl_4$, is only known in double salts. *Ruthenious oxide*, RuO, the *sesquioxide*, Ru_2O_3, and *dioxide*, RuO_2, are black powders, insoluble in acids, and are obtained when ruthenium is roasted in the air.

The *hydroxides*, $Ru_2(OH)_6$ and $Ru(OH)_4$, are produced by the action of the alkalies upon the corresponding chlorides, and are very readily soluble in acids. *Ruthenic acid*, H_2RuO_4, is not known in a free condition. Its potassium salt, K_2RuO_4, is formed by fusing the metal with potassium hydroxide and niter or by digesting the tetroxide with dilute alkali at 60° until the evolution of oxygen ceases:

$$RuO_4 + 2KOH = K_2RuO_4 + H_2O + O.$$

It crystallizes in black prisms with a green luster. It contains one molecule of water of crystallization. It absorbs moisture and carbon dioxide with avidity from the air. Its deep orange-red, dilute, aqueous solution gradually, on exposure to the air, becomes green and a perruthenate results. At the same time a black oxide of the formula Ru_2O_5 separates. This decomposition is more rapid when the solution is acted upon with carbon dioxide, dilute acids, chlorine or bromine. Potassium ruthenate therefore behaves like potassium manganate (p. 390). When chlorine is conducted through a concentrated solution of potassium ruthenate, or when ruthenium is roasted at 1000° in a current of oxygen, *ruthenium tetroxide*, RuO_4, and dioxide are formed. By the chlorine method it volatilizes and may be collected in a well-cooled receiver. It consists of a gold-yellow crystalline mass. It fuses at 25.5°, therefore in the hand, to a deep orange-red colored liquid. It readily sublimes in large, yellow transparent crystals with an orange-yellow reflex. At the ordinary pressure it does not boil at 106°, but it decomposes with explosion at 108°. It can be gasified without decomposition under diminished pressure. Its vapors then correspond to the formula RuO_4. The tetroxide dissolves slowly in water with a golden-yellow color, but does not yield a hydrate. Black compounds of varying composition separate from this solution. *Potassium perruthenate*, $KRuO_4$, is formed along with the more soluble ruthenate on adding the tetroxide to caustic potash.

It crystallizes in black octahedra with metallic luster; they dissolve in water with a deep-green color [see Debray and Joly, Jahresber. der Chemie (1888), 669, 672].

Osmium is very much like ruthenium. It is not even fusible in the oxyhydrogen flame; it only sinters together. According to Violle it fuses at 2500°. Of all the platinum metals it is the most difficult to fuse, but is the most easily oxidized. *Compact osmium is the heaviest metal specifically* (specific gravity 22.48) and is insoluble in aqua regia. Reduced to a fine powder it will burn when ignited in the air to OsO_4. Nitric acid and aqua regia convert it into the same oxide. The compounds, $OsCl_2$ and OsO, $OsCl_3$ and Os_2O_3, OsO_2 and $OsCl_4$, are very similar to the corresponding ruthenium derivatives. By fusion with potassium hydroxide and niter we get *potassium osmate*, K_2OsO_4, which crystallizes from aqueous solution with two molecules of water in dark-violet octahedra. The most stable and a very characteristic derivative of osmium is the *tetroxide*, OsO_4, which is produced by igniting the metal in the air, or by the action of chlorine on osmium in the presence of water. It crystallizes in large colorless prisms, which fuse below 100° and distil at a somewhat higher temperature. It has a very sharp, piercing odor (ὀσμή, odor), similar to that of sulphur chloride. It dissolves slowly but copiously in water; the solution is not acid. Reducing and organic substances precipitate pulverulent osmium from it. This is the basis of its application in microscopy.

OsO_4 and RuO_4 do not afford corresponding salts.

RHODIUM AND IRIDIUM.

Rh = 103.0. Ir = 193.0.

These metals are lighter in color and are more easily fusible than ruthenium and osmium. (Iridium fuses at 1950°.) When pure they are not attacked by acids or aqua regia; but dissolve in the latter when alloyed with platinum.

Rhodium, discovered by Wollaston in 1803, forms three oxides:

$$RhO, Rh_2O_3 \text{ and } RhO_2,$$

of which the second forms salts with acids. RhO_2 results when rhodium is heated with niter.

Of the chlorides only $RhCl_3$ is known. It results when the metal is heated in chlorine gas. It is a brownish-red mass. It forms readily crystallizing, red-colored (hence its name, from ῥοδόεις, rose-red) double salts with alkaline chlorides.

Iridium, discovered in 1804 by Tennant, has perfectly analogous derivatives:

$$IrO, Ir_2O_3, IrO_2, \text{ and } IrCl_2, IrCl_3, IrCl_4.$$

The *sesquichloride*, Ir_2Cl_6, formed by heating iridium in chlorine, is an olive-green, crystalline mass, insoluble in water and acids. It affords double salts with the alkaline chlorides, *e.g.*:

$$K_3IrCl_6 + 3H_2O,$$

which crystallizes from water in green or brown crystals. They are also produced by the action of sulphur dioxide upon the double salts of hydrochloridic acid.

Iridium Tetrachloride, $IrCl_4$, is produced in the solution of iridium or its oxide in aqua regia, and remains, on evaporation, as a black mass, readily soluble in water (with red color) to hydrochloriridic acid:

$$H_2IrCl_6.$$

When alkaline chlorides are added to the solution double chlorides are precipitated, *e.g.*:

$$(NH_4)_2IrCl_6, K_2IrCl_6,$$

isomorphous with the corresponding double chlorides of platinum. When a solution of $IrCl_4$ is boiled with caustic potash, $Ir(OH)_4$ will be precipitated. The name *iridium* alludes to the differently colored compounds yielded by the metal.

PALLADIUM.

Pd — 106.

Palladium, in addition to occurring in platinum ores, is found alloyed with gold (Brazil), and in some selenium ores (Hartz); it has a silver-white color, and is somewhat more fusible (at about 1400°) than platinum. When finely divided it dissolves in boiling concentrated hydrochloric, sulphuric, and nitric acids. When ignited in the air it at first becomes dull by oxidation, but at a higher temperature the surface again assumes a metallic appearance. It was discovered in 1803 by Wollaston and named after the planet *Pallas*, which had been found shortly before.

Palladium absorbs hydrogen gas (occlusion) to a much greater extent than platinum or silver. Freshly ignited palladium leaf absorbs upwards of 370 volumes of hydrogen at ordinary temperatures, and about 650 volumes at 90–100°. A greater absorption may be effected at ordinary temperatures in the following manner:

Water is decomposed by the electric current, palladium foil being used as a negative electrode. The liberated hydrogen is then taken up by the palladium (to 960 volumes); the metal expands ($\frac{1}{10}$ its volume), becomes specifically lighter, but retains its metallic appearance entire. According to the investigations of Debray, the compound Pd_4H_2 is produced, which contains dissolved hydrogen, and deports itself similarly to an alloy. Recent investigations show that palladium hydride is a so-called "solid solution" of hydrogen in palladium (pp. 46, 256). Palladium charged with hydrogen usually remains unaltered in the air, and in a vacuum; it, however, sometimes becomes heated in the air, as the hydrogen is oxidized to water. The same occurs when palladium hydride is heated to 100°; *in vacuo*, all the hydrogen escapes as gas. Palladium hydride is a strong reducing agent, like nascent hydrogen. Ferric salts are reduced to the ferrous state; chlorine and iodine in aqueous solution are converted into hydrochloric and hydriodic acids.

Palladium black absorbs hydrogen more energetically than the compact variety (at 100° upwards of 980 volumes). This substance is obtained by the reduction or electrolysis of palladic chloride. If palladium sponge be heated in the air until the white metallic color becomes black, in consequence of the superficial oxidation, it will absorb hydrogen very energetically at ordinary temperatures, and partly oxidize it to water.

When palladium-sheet or sponge is introduced into the flame of a spirit-lamp, it is covered with soot; this is due to the fact that the metal withdraws the hydrogen of the hydrocarbons, and carbon is set free.

There are two series of palladium compounds: the *palladious*, PdX_2, and *palladic*, PdX_4. The first are well characterized and are distinguished by their stability.

Palladious Chloride, $PdCl_2$, remains as a brown, deliquescent mass, on evaporating the solution of palladium in aqua regia. It yields easily soluble crystalline double salts, with alkaline chlorides, *e.g.*, $PdCl_2 . 2KCl = K_2PdCl_4$.

Palladious Iodide, PdI_2, is precipitated from palladious solutions by potassium iodide as a black mass, insoluble in water. As palladium chloride and bromide are very soluble in water, palladium salts can be used to detect iodine in the presence of hydrobromic or hydrochloric acid.

Palladious Oxide, PdO, is a black residue left upon careful ignition of the nitrate. It is difficultly soluble in acids. When heated, it loses oxygen, and forms *palladium suboxide*, Pd_2O.

When palladium is dissolved in sulphuric or nitric acids, the corresponding salts are produced.

The **sulphate**, $PdSO_4 + 2H_2O$, is composed of brown crystals, readily soluble in water. Much of the latter decomposes it.

Palladic Chloride, $PdCl_4$, *Hydrochlorpalladic Acid*, H_2PdCl_6, is formed when the metal is dissolved in aqua regia. They decompose, on evaporation, into $PdCl_2$ and Cl_2. When potassium or ammonium chloride is added to their solutions, red-colored difficultly soluble double chlorides crystallize out; they are analogous to the corresponding salts of platinum.

PLATINUM.

Pt = 194.8.

The separation of platinum from the ore was described on p. 409. (See Mylius and Foerster, Ber. **25** (1893), 665.) The metal has a grayish-white color, and a specific gravity of 21.4. It is very tough and malleable, and may be drawn out into very fine wire and rolled into foil. At a high heat it softens without melting, and may be easily welded. It fuses in the oxyhydrogen flame (at about 1770°—Violle), and is somewhat volatile. On fusion, it absorbs oxygen, which it gives up again on cooling (like silver). At ordinary temperatures, it also condenses hydrogen and oxygen upon its surface; as foil and sponge, but very few volumes; as platinum black, about 100 times its volume of oxygen and 310 times its volume of hydrogen. Two hundred volumes of the latter form water with the oxygen always present in the sponge (Z. f. anorg. Ch. **10** (1895), 178). These gases are fully expelled at a red heat. Platinum sponge is obtained as a fine black powder, if reducing substances, like zinc, be added to solutions of platinic chloride or upon boiling the solution with sugar and sodium carbonate; it remains on the ignition of $PtCl_4 . 2NH_4Cl$. The production of various reactions is due to the power of platinum to condense oxygen; thus hydrogen will inflame in the air, if it be conducted upon platinum sponge; sulphur dioxide combines with oxygen at 100° to form the trioxide. At a red heat platinum permits free passage to hydrogen, while it is not permeable by oxygen and other gases (p. 93).

Platinum is not attacked by acids; it is only soluble in liquids generating free chlorine, *e. g.*, aqua regia. In consequence of this resistance to acids, and its unalterability upon ignition, this metal answers as an undecomposable material for the production of chemical crucibles, dishes, wire, etc. The usual presence of iridium in ordinary platinum increases its durability.

The alkaline hydroxides, sulphides, and cyanides attack it strongly at a red heat. It forms readily fusible alloys with phosphorus, arsenic, and many heavy metals, especially lead, and many heavy metals are reduced from their salts by platinum. Therefore such substances must not be ignited in platinum crucibles, etc.

Platinum, like palladium, forms *platinous*, PtX_2, and *platinic*, PtX_4, derivatives; in the first it is more basic, in the latter more acidic.

Platinic Chloride, $PtCl_4$, is obtained by the solution of platinum in aqua regia, and when the liquid is evaporated with an excess of hydrochloric acid, *hydrochlorplatinate*,

$$PtCl_4 . 2HCl = H_2PtCl_6,$$

crystallizes with six molecules of water in brownish-red, deliquescent prisms. It forms characteristic double chlorides,

$$PtCl_4 . 2KCl,$$

with ammonium and potassium chlorides. They are the *chlorplatinates.* Formerly they were considered double salts. They are difficultly soluble in water; hence, on mixing the solutions, they immediately separate out as a crystalline yellow powder. Ignition completely decomposes the ammonium salt, leaving spongy platinum.

Platinum chloride yields similar insoluble salts with the chlorides of rubidium, cæsium, and thallium, while that with sodium,

$$Na_2PtCl_6 + 6H_2O,$$

is very soluble in water. Platinum may be very readily separated from other metals by recrystallizing the sodium salt from hot water rendered alkaline by soda (Finkener).

On adding sodium hydroxide to platinic chloride and then supersaturating with acetic acid, there separates a reddish-brown precipitate of *platinic hydroxide*, $Pt(OH)_4$. This dissolves readily in acids (excepting acetic), with formation of salts. The oxygen salts, as $Pt(SO_4)_2$, are very unstable. The hydroxide has also an acidic character (*platinic acid*), and dissolves in alkalies, yielding salts with them. These, also, result on fusing platinum with potassium and sodium hydroxide. The barium salt,

$$Pt\left\{\begin{matrix}(OH)_2\\ O_2Ba\end{matrix}\right. + 3H_2O,$$

is precipitated from platinic chloride, by barium hydroxide, as a yellow, crystalline compound. The acidic nature of its hydroxide allies platinum to gold. If hydrogen sulphide be conducted through platinic solutions, black *platinum disulphide*, PtS_2, is precipitated; it is soluble in alkaline sulphides, with formation of sulpho-salts.

Platinous Chloride, $PtCl_2$, is a green powder, insoluble in water, remaining after heating platinic chloride to 200°. It forms double salts with alkaline chlorides, *e. g.:*

$$PtCl_2 . 2NaCl.$$

When digested with potassium hydroxide it yields the hydroxide, $Pt(OH)_2$.

Cyanogen Compounds.—Like cobalt, platinum forms double cyanides corresponding to the ferrocyanides. When platinous chloride is dissolved in potassium cyanide *platinum potassium cyanide*, $K_2Pt(CN)_4 + 4H_2O$, crystallizes on evaporation in large prisms exhibiting magnificent dichroism; in transmitted light they are yellow and in reflected light blue. This salt must be viewed as the potassium compound of *hydroplatino-cyanic acid*, $H_2Pt(CN)_4$. When separated from its salts it crystallizes in gold-yellow needles. Its salts with heavy metals are obtained by double decomposition, and all show a beautiful play of colors. The barium salt, barium platino-cyanide, $BaPt(CN)_4 + 4H_2O$, is used to render the Röntgen rays visible.

Platinum-ammonium Compounds.—There is a whole series of these, which must be viewed as platinum bases and their salts. They are constituted according to the following empirical formulas:

(*a*) Platosamines (platinous series):

$$PtR_2(NH_3); \quad PtR_2(NH_3)_2; \quad PtR_2(NH_3)_3; \quad PtR_2(NH_3)_4.$$

(*b*) Platinamines (platinic series):

$$PtR_4(NH_3); \quad PtR_4(NH_3)_2; \quad PtR_4(NH_3)_3; \quad PtR_4(NH_3)_4.$$
$$(R = OH, Cl, Br, I, NO_3, \text{etc.}).$$

Diplatosamine derivatives, *e. g.*, $(NH_3)_4Pt_2R_2$, are also known. They evidently contain radicals or ions, consisting of platinum, the group NH_3, and halogens (also NO_3, etc.). They result from the action of ammonia upon platinous chloride. When the acid residues are replaced by hydroxyl groups platinum bases are formed, *e. g.*, $Pt(NH_3)_4(OH)_2$, which resemble alkaline hydroxides in their chemical properties. The other platinum metals form similar amine derivatives. The nature and chemical constitution of these interesting compounds is, however, not fully explained.

SPECTRUM ANALYSIS.[*]

We observed that many substances, when introduced into a non-luminous flame, imparted to it a characteristic coloration. Thus, the sodium

---

[*] A more exhaustive, concise, and distinct presentation of the spectrum phenomena may be found in Herman W. Vogel's "Praktische Spektralanalyse irdischer Stoffe," 1889, and in "Lehrbuch der Spektralanalyse," by H. Kayser, 1883.

compounds color it yellow; the potassium, violet; thallium, green, etc. The decomposition of the light thus obtained, and, indeed, of every light, by means of a prism, and the study of the resulting spectrum, form the basis of spectrum analysis, established in 1859 by Kirchhoff and Bunsen.

Every substance, solid or liquid, heated to white heat (*e. g.*, molten platinum; lime heated in the oxyhydrogen flame; the ordinary flame containing glowing particles of carbon) emits rays of every refrangibility; and hence furnishes a *continuous spectrum*, which brings to view all the colors of the rainbow, from red to violet, if the light be conducted through a prism. Glowing gases and vapors, on the contrary, whose molecules can execute unobstructed oscillations, emit light of definite refrangibility, and, therefore, give spectra, consisting of single, bright lines. Thus, the spectrum of the yellow sodium flame is recognized as composed of one very bright yellow line, which by increased magnifying power is shown to consist of two lines lying very near each other. The violet potassium light gives a spectrum, consisting of a red and a blue line. The crimson strontium light shows in the spectrum several distinct red lines and a blue line. (See the Spectrum Plate.) Each of these lines corresponds to rays of definite wave-length, which are differently refracted from all the others; hence the lines appear in the same spectrum at the same point, when rays of their wave-length fall on the slit.

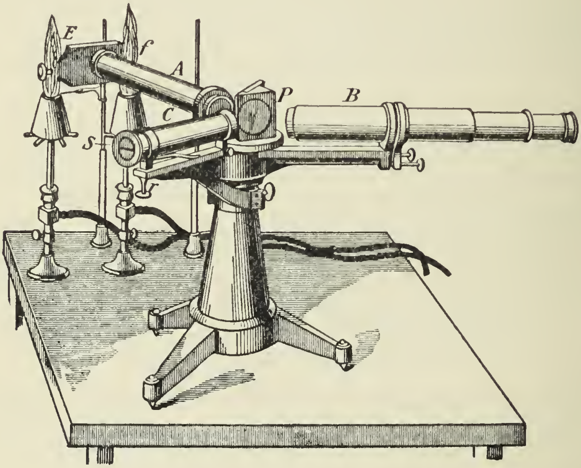


FIG. 69.

If substances affording different colors be introduced into a flame, the most intense color generally obscures the others; in the spectrum, however, each individual substance shows its peculiar bright lines, which appear simultaneously or succeed each other, according to the volatility of the various substances.

The spectrum apparatus or spectroscope, shown in Fig. 69, serves for the observation of the spectra.

In the middle of the apparatus is a flint-glass prism *P*. At the further end of the tube *A* is a movable vertical slit, in front of which is placed the light to be investigated. The entering light rays are directed by a collecting lens into the tube *A*, upon the prism, and the refracted rays (the spectrum) are observed by the telescope *B*. The tube *C* is employed to ascertain the relative position of the spectrum lines. This is provided at the outer end of the tube *S* with a transparent horizontal scale. When a luminous flame is placed before the scale its divisions are reflected from the prism surface and thrown into the telescope *B*. We then see the spectrum to be studied and the scale divisions in *B* at the same time, and can readily determine the relative position of the lines of the spectrum. To study two spectra at the same time, and compare them, a three-sided, right-angled glass prism is attached in front of one-half (the lower or upper) of the slit of the tube *A*; this directs the rays of a light placed at the side (*f*, Fig. 69) through *A* upon the prism *P*. By means of *B*, two horizontal spectra will be observed, one above the other, and between are the bright divisions of the scale.

Adjustment of the Spectroscope.—To observe the spectra in the apparatus described, it is necessary first to adjust the same correctly. The tube *A* (objective or collimator tube) contains, besides the slit, also a lens (collimator lens), which serves to render parallel the bunch of rays proceeding from the slit; hence, the latter must be accurately placed in the focus of the lens. This is best accomplished as follows: The telescope (*B*) is drawn out and adjusted for some distant object, that it may be adapted for the reception of parallel rays; observe the slit illuminated by the sodium chloride flame, and change its position with reference to the collimator lens until its image appears sharply defined in the telescope *B*. The scale in tube *S* is similarly adjusted. To have the spectrum lines sharply defined, the slit must be made quite narrow; for feebly luminous lines it must, however, be widened.

The *determination of the position of the lines of the spectra* is usually effected by means of a scale. Since the refraction and dispersion of the rays and therefore the expansion of the spectrum and the length-relations of its variously colored parts are influenced by the angle and the quality of the glass of the prism, the scale indications of different forms of apparatus are not directly comparable. To attain this it is ordinarily sufficient to indicate how the most important Fraunhofer lines (see below) are divided upon the scale.

The spectra represented on the plate are then produced by the frequently mentioned colors shown by compounds of the alkali and alkaline earth metals when heated in the non-luminous flame of the Bunsen burner.

The other metals, however, require a much higher temperature than that of the gas flame for their conversion into gases. To vaporize them and observe their spectra, the electric spark is made to pass from electrodes constructed of them. A very convenient and universally applicable procedure consists in passing the sparks between the surface of the solution of the salt, into which the negative pole dips, and a platinum wire (positive pole) placed before the slit of the spectroscope [R. Bunsen, Pogg. Ann. (1873) **155**, 230, 336; Z. f. anal. Ch. (1876) **15**, 68, and M. Lecoq de Boisbaudran, Spectres lumineux, Paris, 1874]. Many of the metal spectra, obtained in this way, are remarkably rich in lines. Thus, over 450 lines have been established for iron.

The spectra of the gases may be obtained by means of the Geissler tubes. The latter contain the gas in a rarefied condition and they give their own peculiar colors on passing induction sparks through them. Hydrogen gives a red light; its spectrum consists of a bright red, a blue, and a green line. Nitrogen gives a violet light and affords a spectrum of many lines and bands.

These methods give us a means for readily distinguishing the individual chemical elements, and even detecting them in traces. Since the year 1860 various new elements, *e. g.*, cæsium, rubidium, thallium, indium, scandium, gallium, germanium, and several others, not accurately studied, have been discovered by their aid. Argon, helium and the other substances discovered recently in the air are especially distinguished by their spectra.

In addition to the bright *emission spectra* just described there are yet *dark absorption spectra.* If a white light giving an uninterrupted spectrum be allowed to pass through different transparent bodies, the latter will absorb rays of definite refrangibility, allowing all others to pass. Therefore we observe the sun spectrum interrupted by dark lines or bands in the spectroscope. The solutions of didymium and erbium absorb certain rays, and show corresponding dark lines in the spectrum. The gases deport themselves similarly. White light that has traversed a broad layer of air shows several dark lines in the spectrum; the air absorbed the corresponding rays. This power of absorption is possessed to a much higher degree by all incandescent gases or vapors. If a white light, like the Drummond calcium light, be conducted through the yellow sodium flame (through glowing sodium vapors), a dark line will appear in the spectrum of the white light, and its position will correspond exactly to that of the yellow sodium line; the latter thus appears converted into a dark line. Such spectra are designated the *inverted spectra* of the corresponding metals. The inverted spectra of all elements may be obtained in this way, and they correspond accurately to the direct bright spectra. The cause of these phenomena lies in the proposition deduced by Kirchhoff from the undulatory theory of light, *that the ratio between the emissive and absorptive power is the same for almost all bodies at like temperatures.* According to this incandescent gases only absorb rays of just the same refrangibility as those which they emit. For example, when bright white light is passed through the yellow sodium flame the yellow rays of the former are absorbed and retained, while all others pass on almost entirely unaltered. Therefore, in the rainbow spectrum of white light the yellow rays of definite refrangibility will be absent; and if the other refracted rays of the white light are brighter than the yellow rays emitted from the sodium flame, the latter will be relatively darker; a dark line will therefore make its appearance.

These phenomena have presented a new and wide province to spectral analysis, inasmuch as they open up avenues for the investigation of the chemical nature of the sun and other bodies.

It is known that the bright rainbow sun spectrum is intersected by a number of dark lines which have been called the Fraunhofer lines from their discoverer. Kirchhoff has shown that these lines can be easily accounted for, after what has already been said, by the following hypothesis upon the nature of the sun: The latter consists of a solid or liquid luminous nucleus, surrounded by an atmosphere of incandescent gases and vapors. Then the uninterrupted spectrum of the glowing nucleus must be intersected by the dark lines of the inverted spectra of those gases and vapors which occur in the sun's atmosphere. An accurate comparison of the Fraunhofer lines with the spectrum lines of the various elements has revealed the fact that iron, sodium, magnesium, calcium, chromium, nickel, barium, copper, zinc, and hydrogen are present in the sun's atmosphere. Thus dark lines have been found in the sun's spectrum corresponding to all of the 450 lines of the iron spectrum. According to Rowland 34 of the elements known to us are present in the sun; 15 are absent, and much doubt prevails as to the presence of the remainder. Helium, first discovered in the earth in 1895, was known to exist in the sun's photosphere since 1868. The inferences upon the chemical constitution of the sun possess as much and, indeed, a higher degree of probability than falls to many other deductions.

All the fixed stars thus far investigated possess a constitution like that of the sun. They give spectra intersected by dark lines, and therefore consist of incandescent nuclei surrounded by gaseous atmospheres. The spectra of nebulæ, however, only show bright lines; hence these consist of uncondensed, incandescent masses of vapor.

INDEX.

A Catalogue of Books on Chemistry, Technology, Water and Milk Analysis, Hygiene, Toxicology, etc., Published by P. Blakiston's Son & Co., 1012 Walnut Street, Philadelphia

INDEX OF SUBJECTS.

☞ The Prices given in this Catalogue are absolutely net. No discount whatever can be allowed retail purchasers.

P. Blakiston's Son & Co.'s publications may be had through Booksellers in all the principal cities of the United States and Canada. Any book will be sent, postpaid, upon receipt of price, or will be forwarded by express, C. O. D., if preferred. Money should be remitted by postal note, express money order, registered letter, or bank draft.

Complete catalogues of Books on Medicine, Dentistry, Hygiene, Nursing, and Pharmacy will be sent free upon application.

Cat. 4—7-27-1900

ALLEN'S
Commercial Organic Analysis.
AUTHORIZED REVISED EDITIONS.

A Treatise on the Properties, Proximate Analytical Examination and Modes of Assaying the Various Organic Chemicals and Products employed in the Arts, Manufactures, Medicine, etc., with Concise Methods for the Detection and Determination of Impurities, Adulterations and Products of Decomposition, etc. Revised and Enlarged.

BY ALFRED H. ALLEN, F.I.C., F.C.S.,

Public Analyst for the West Riding of Yorkshire and the City of Sheffield;
Past President of the Society of Public Analysts of Great Britain, etc.

We are pleased to announce that Mr. Allen has authorized us to reprint those volumes of this well-known work which have been out of print for a number of years, and has given to Dr. Henry Leffmann, of Philadelphia, the right to make such addenda and editoral notes as are necessary to bring the books up to date. Mr. Allen has himself furnished much material and has aided the editor in every possible way.

Vol. I. Preliminary Examination of Organic Bodies. Alcohols, Neutral Alcoholic Derivatives, Ethers, Starch and its Isomers, Sugars, Acid Derivatives of Alcohols and Vegetable Acids, etc. Third Edition, with numerous additions by the author, and revisions and additions by Dr. HENRY LEFFMANN. With many useful tables. Cloth, $4.50

Vol. II—Part I. Fixed Oils, Fats, Waxes, Glycerin, Soaps, Nitroglycerin, Dynamite and Smokeless Powders, Wool-Fats, Dégras, etc. Third Edition, with many useful tables. Revised by DR. HENRY LEFFMANN, with numerous additions by the Author. Cloth, $3.50

Vol. II—Part II. Hydrocarbons, Mineral Oils, Lubricants, Asphalt, Benzene and Naphthalene, Phenols, Creosote, etc. Third Edition, by DR. HENRY LEFFMANN, with many additions by the Author. Cloth, $3.50

Vol. II—Part III. Terpenes, Essential Oils, Resins, Camphor, Aromatic Acids, etc. Third Edition, Revised by the Author and DR. HENRY LEFFMANN. *Preparing.*

Vol. III—Part I. Tannins, Dyes, Coloring Matters, and Writing Inks. Third Edition, revised by J. MERRITT MATTHEWS, PH.D., Professor of Chemistry and Dyeing at the Philadelphia Textile School; Member of the Society of Dyers and Colorists of England; Member of American Chemical Society, etc. *Nearly Ready.*

Vol. III—Part II. The Amines and Ammonium Bases, Hydrazines and Derivatives. Bases from Tar. The Antipyretics, etc. Vegetable Alkaloids, Tea, Coffee, Cocoa, Kola, Cocaine, Opium, etc. Second Edition, with numerous addenda. Cloth, $4.50

Vol. III—Part III. Vegetable Alkaloids concluded, Non-Basic Vegetable Bitter Principles. Animal Bases, Animal Acids, Cyanogen and its Derivatives, etc. Second Edition. Cloth, $4.50

Vol. IV. The Proteids and Albuminous Principles. Proteoïds or Albuminoïds. Second Edition, with elaborate appendices and a large number of useful tables. Cloth, $4.50

NEW EDITIONS

RICHTER'S CHEMISTRIES.

AUTHORIZED TRANSLATIONS.

BY EDGAR F. SMITH, M.A., PH.D., SC.D.,

Professor of Chemistry in the University of Pennsylvania; Member of the Chemical Society of Berlin, American Philosophical Society, etc., etc.

Professor Richter's methods of arrangement and teaching have proved their superiority by the large sale of his books throughout Europe and America, translations having been made in Russia, Holland, and Italy. The success attending the publication in this country could only have been attained for good books that have been found useful, practical, and thoroughly up to the times.

THE CHEMISTRY OF THE CARBON COMPOUNDS, or Organic Chemistry. Third American, translated from the Eighth German Edition by PROF. R. ANSCHÜTZ, University of Bonn. Thoroughly Revised, Enlarged, and in many parts Rewritten. Illustrated. Two Volumes. 12mo.

Vol. I. Aliphatic Series. 625 pages. Cloth, $3.00

Vol. II. Carbocyclic and Heterocyclic Series. 671 pages. Cloth, $3.00

From Science.

"Anschütz, in editing v. Richter's 'Organic Chemistry,' has raised it from the rank of a good descriptive manual to a place in the front rank of books on this subject. He has had the aid of Emil Fischer in the supervision of the chapters on the carbohydrates and on uric acid; of v. Baeyer, Claisen, Waitz, and others on the work in their respective fields. The introduction occupies 77 pages, and among other subjects includes condensed presentations of the aims of physical chemistry and stereochemistry, of the work based on the optical and magnetic properties of carbon compounds, and of that based on measurements of conductivity. **The book is written tersely and clearly.** The nomenclature in common use is retained, but that recommended by the Geneva Conference is also given. The literature and historical references are abundant. . . . The volume before us **contains the results of the latest work** on the subject, and, as the second (and last) volume on the aromatic series is promised by the publishers during the present year, the student purchasing this excellent book may feel confident that he has the last word on the subject up to the date of publication."

From The Journal of the Worcester Polytechnic Institute.

"We can unhesitatingly recommend it as the best work of its kind in our language."

From The Lancet, London.

"We doubt whether there is a chemist living whose opinions on organic chemistry are more respected than those of Richter. . . . It teems with facts and contains an explicit account of the theory of the science and the architecture of the complex organic molecules."

INORGANIC CHEMISTRY. Fifth American from the Tenth German Edition by PROF. H. KLINGER, University of Königsberg. Thoroughly Revised and in many parts Rewritten. With many Illustrations and Colored Plate of Spectra. 12mo.

Cloth, $1.75

From The Scientific American.

"It is markedly practical, clear, and direct in its statements, bringing out prominently the relations between proved facts and theories or hypotheses, so as to preclude as far as possible speculative inferences from the mind of a student beginning the study of chemistry."

CONGDON. Laboratory Instructions in General Chemistry. By ERNEST A. CONGDON, Professor of Chemistry in the Drexel Institute, Philadelphia; Member American Chemical Society; Fellow London Chemical Society, etc. Illustrated.

In Press.

ULZER AND FRAENKEL. Introduction to Chemical-Technical Analysis. By Prof. F. ULZER and DR. A. FRAENKEL, Directors of the Testing Laboratory of the Royal Technological Museum, Vienna. Authorized Translation by HERMANN FLECK, NAT.SC.D., Instructor in Chemistry in the John Harrison Laboratory of Chemistry, University of Pennsylvania. With an Appendix by the Translator relating to Food-Stuffs, Asphaltum, and Paint. 12 Illustrations. 8vo. Cloth, $1.25

With a view to increasing its usefulness as a text-book and laboratory guide, the translator has added descriptions of the analysis of typical food-stuffs and other important products.

BLOXAM. Chemistry—Inorganic and Organic. With Experiments. By CHARLES L. BLOXAM. Edited and Revised by J. M. THOMPSON, Professor of Chemistry in King's College, London, and A. G. BLOXAM, Head of Chemistry Department, The Goldsmith Institute, London. Eighth Edition, Enlarged. 281 Engravings, 20 of which are new. 8vo. Cloth, $4.25; Leather, $5.25

This—the eighth—edition has been very thoroughly revised. Many changes have been made, though the general arrangement remains the same. The sections on explosives, to which the work owes considerable reputation, have been carefully gone over. It is in some respects more thorough and complete than any other work.

BARTLEY. Medical and Pharmaceutical Chemistry. By E. H. BARTLEY, M.D., Professor of Chemistry and Toxicology at the Long Island College Hospital; Dean and Professor of Chemistry, Brooklyn College of Pharmacy; Chief Chemist, Board of Health of Brooklyn. Fifth Edition, Revised and Enlarged. 92 Illustrations and Glossary. 12mo. Cloth, $3.00

"This excellent book contains, in the most concise form, all the knowledge of medical and pharmaceutical chemistry. The present edition has been greatly enlarged, and a new chapter on Physiological and Clinical Chemistry added. . . . The whole book reads admirably well and deserves the highest recommendation."—*N. Y. Medical Record.*

Clinical Chemistry. The Chemical Examination of the Saliva, Gastric Juice, Feces, Milk, Urine, etc., with notes on Urinary Diagnosis, Volumetric Analysis, and Weights and Measures. Illustrated. 12mo. Cloth, $1.00

TRAUBE. Physico-Chemical Methods. By DR. J. TRAUBE, Privatdocent in the Technical High School of Berlin. Authorized Translation by W. L. HARDIN, PH.D., Instructor in Chemistry, University of Pennsylvania. 97 Illustrations. 8vo. Cloth, $1.50

"Dr. Traube's book should certainly be welcomed by us all on account of the clear and concise exposition he has given us of the most important of physico-chemical methods. The value of this book is further enhanced by a number of good cuts which aid one in obtaining a clear idea of the methods under discussion. The book has been carefully edited, and the typography is good."—*The Journal of the Worcester Polytechnic Institute.*

CALDWELL. Chemical Analysis. Elements of Qualitative and Quantitative Chemical Analysis. By G. C. CALDWELL, B.S., PH.D., Professor of Agricultural and Analytical Chemistry in Cornell University, Ithaca, New York, etc. Third Edition. Revised and Enlarged. Octavo. Cloth, $1.50

This book has been extensively used in American Schools and Colleges, and needs no special introduction. Written to supply Prof. Caldwell's need in his own work, it is an eminently practical and complete text-book.

HOLLAND. The Urine, the Gastric Contents, the Common Poisons, and the Milk. Memoranda, Chemical and Microscopical, for Laboratory Use. By J. W. HOLLAND, M.D., Professor of Medical Chemistry and Toxicology in Jefferson Medical College, Philadelphia. Sixth Edition, Enlarged. Illustrated and Interleaved. 12mo. Cloth, $1.00

LEFFMANN. Compend of Medical Chemistry, Inorganic and Organic. Including Urine Analysis, Chemistry of Tissues and Secretions, Table of Symbols, Valencies, Atomic Weights, etc. By HENRY LEFFMANN, M.D., Professor of Chemistry and Metallurgy in the Pennsylvania College of Dental Surgery and in the Wagner Free Institute of Science, Philada.; Professor of Chemistry, Woman's Medical College of Pennsylvania, etc. Fourth Edition. Cloth, .80; Interleaved for the addition of Notes, $1.25

The Coal-Tar Colors, with Special Reference to their Injurious Qualities and the Restrictions of their Use. A Translation of Theodore Weyl's Monograph. 12mo. Cloth, $1.25

Structural Formulæ for the Use of Students. Containing 180 Structural and Stereo-Chemic Formulæ. 12mo. Interleaved. Cloth, $1.00

⁂ See also Water and Milk Analyses, page 10.

CLOWES AND COLEMAN. Quantitative Analysis. Adapted for the Use of the Laboratories of Schools and Colleges. By Frank Clowes, sc.d., Emeritus Professor of Chemistry, University College, Nottingham, and I. Bernard Coleman, Assoc. R. C. Sci., Dublin, Professor of Chemistry, Southwest London Polytechnic. Fifth Edition. 117 Illustrations. *Nearly Ready.*

OETTEL. Practical Exercises in Electro-Chemistry. By Dr. Felix Oettel. Authorized Translation by Edgar F. Smith, m.a., Professor of Chemistry, University of Pennsylvania; Translator of Richter's Chemistries, etc. Illustrated. Cloth, .75

Introduction to Electro-Chemical Experiments. Illustrated. By same Author and Translator. Cloth, .75

SMITH. Electro-Chemical Analysis. By Edgar F. Smith, Professor of Chemistry, University of Pennsylvania. Second Edition. Enlarged. 28 Illustrations. 12mo. Cloth, $1.25

⁂ This book has recently been translated into German by Dr. Max Ebeling of Berlin, and into French by Prof. J. Rosset.

"The greatest advantage of the electrolytic method of analysis is its simplicity. We do not require to introduce materials the purity of which often leaves something to be desired, and which have to be again removed, frequently at the cost of much time and trouble. Hence, where available, the electrolytic method of analysis possesses an indisputable advantage. We hope that Prof. Smith's little work will call increased attention to this branch of mineral analysis."—*Chemical News, London.*

"Chemists will find this little book an excellent guide to a knowledge of the methods of quantitative analysis by electrolysis."—*American Chemical Journal, Baltimore, Md.*

MUTER. Practical and Analytical Chemistry. By John Muter, f.r.s., f.c.s., etc. Second American from the Eighth English Edition. Revised to meet the requirements of American Medical, Pharmaceutical, and Dental Colleges. 56 Illustrations. Cloth, $1.25

"The editor has made only such changes as were required to adapt the book to the U. S. Pharmacopœia, except in the chapter on urine analysis, which has been enlarged and to which cuts of microscopic sediments and other illustrations have been added. Several other processes have been added, such as estimation of chloral hydrate, of fat in milk, etc."—*The Popular Science Monthly.*

TYSON. Guide to the Practical Examination of Urine. Ninth Edition. By James Tyson, m.d., Professor of Medicine, University of Pennsylvania, etc. With Colored Plate and 48 Illustrations. Ninth Edition. 12mo. 276 pages. Cloth, $1.25

The prices of these books are net. No discount allowed retail purchasers.

SMITH AND KELLER. Experiments. Arranged for Students in General Chemistry. By EDGAR F. SMITH, Professor of Chemistry, University of Pennsylvania, Translator of Richter's Chemistries, etc., and Dr. H. F. KELLER, Professor of Chemistry, Philadelphia High School. Third Edition. 41 Illus. Cloth, .60

"This series of exercises, based on the authors' experiences with their own classes, is intended to accompany any convenient text-book of inorganic chemistry; but reference is made to that of Richter. Beginning with fundamental operations (as with blowpipe, glass tubing, balance, and graduates) and general principles (as the difference between chemical and physical change), the course proceeds to the study of hydrogen and other non-metals in Part I, followed by the metals in Part II. Quantitative relations are well presented in the experimental work and stoichiometrical problems, as in determining the *H*-equivalent of zinc, the density of *Cl*, eudiometric combustion of methane, etc."—*Science.*

THRESH. Water and Water Supplies. By JOHN C. THRESH, D.SC. (London), M.D., D.PH. (Cambridge), Medical Officer of Health to the Essex County Council; Lecturer on Public Health, King's College, London; Fellow of the Institute of Chemistry, etc. Second Edition, Revised. Illustrated. 12mo. 438 pages. Cloth, $2.00

SUTTON. Volumetric Analysis, a Systematic Handbook of; or, the Quantitative Estimation of Chemical Substances by Measure, applied to Liquids, Solids, and Gases. Adapted to the requirements of Pure Chemical Research, Pathological Chemistry, Pharmacy, Metallurgy, Manufacturing Chemistry, Photography, etc., and for the Valuation of Substances used in Commerce, Agriculture, and the Arts. By FRANCIS SUTTON, F.C.S., F.I.C., Public Analyst for the County of Norfolk. Eighth Edition. Revised and Improved. 112 Illustrations. *Just Ready.* Cloth, $5.00

"We need only say that this work is welcome as bringing 'Sutton's Volumetric Analysis' down to date. The original book has been so long the standard, and is so well known, that description seems hardly necessary."—*The Scientific American.*

SYMONDS. Manual of Chemistry, for Medical Students. By BRANDRETH SYMONDS, A.M, M.D., Ass't Physician Roosevelt Hospital, Out-Patient Department; Attending Physician Northwestern Dispensary, New York. Second Edition. Cloth, $2.00

SMITH. Dental Metallurgy. A Manual. By ERNEST A. SMITH, F.C.S., Assistant Instructor in Metallurgy, Royal College of Science, London. Illustrated. 12mo. Cloth, $1.75

"The metals in common use in dental practice are each described, and a special chapter is devoted to the question of Dental Amalgams. With a view of rendering the book as practical as possible, the author has enumerated a list of 100 experiments."—*The Lancet, London.*

WOODY. Essentials of Medical and Clinical Chemistry. With Laboratory Exercises. By SAM E. WOODY, A.M., M.D., Professor of Chemistry and Diseases of Children in the Medical Department of Kentucky University, Louisville. Fourth Edition. Revised, with Tables and Illustrations. 12mo. *Nearly Ready.*

TOXICOLOGY AND MED. JURISPRUDENCE.

REESE'S Medical Jurisprudence and Toxicology. A Text-book for Medical and Legal Practitioners and Students. By JOHN J. REESE, M.D., late Professor of the Principles and Practice of Medical Jurisprudence, including Toxicology, in the University of Pennsylvania, Medical Department. Fifth Edition. Revised and Enlarged by HENRY LEFFMANN, M.D., Pathological Chemist, Jefferson Medical College Hospital, Philadelphia; Hygienist and Food Inspector Pennsylvania State Board of Agriculture, etc. 12mo. 646 pages. Cloth, $3.00; Leather, $3.50

"To the student of medical jurisprudence and toxicology it is invaluable, as it is concise, clear, and thorough in every respect."—*The American Journal of the Medical Sciences.*

"The book happily meets the needs of students, and we unqualifiedly commend it."—*American Practitioner and News, Louisville.*

"The book will be found to be a useful one, and as such we commend it to students of law and medicine."—*Marshall D. Ewell, Dean of the Kent Law School, Chicago.*

MANN. Forensic Medicine and Toxicology. A Text-book by J. DIXON MANN, M.D., F.R.C.P., Professor of Medical Jurisprudence and Toxicology in Owens College, Manchester; Examiner in Forensic Medicine in University of London, etc. Illustrated. Octavo. Cloth, $6.50

TANNER'S Memoranda of Poisons and their Antidotes and Tests. By THOS. HAWKES TANNER, M.D., F.R.C.P. Seventh American, from the last London Edition. Revised by JOHN J. REESE, M.D., Professor of Medical Jurisprudence and Toxicology in the University of Pennsylvania. 12mo. Cloth, .75

"The fact of any technical work, great or small, reaching its seventh edition speaks for itself. In the most condensed form are given the history of poisons, their antidotes, and various mechanical methods for overcoming the tendency toward death. The principal changes in the new edition have been the substitution of modern chemical nomenclature and the omission of obsolete portions of the old text. The toxicology of poisonous food has been presented as fully as the concise character of the book allows."—*Medical Record, New York.*

GROVES AND THORP. Chemical Technology. The Application of Chemistry to the Arts and Manufactures. Edited by CHARLES E. GROVES, F.R.S., and WM. THORP, B.Sc., F.I.C. With numerous Illustrations. Each volume sold separately.

Vol. I. **Fuel and Its Applications.** By Dr. E. J. MILLS, F.R.S., Professor of Chemistry, Anderson College, Glasgow; and Mr. F. J. ROWAN, C.E., assisted by an American expert. 607 Illustrations and 4 Plates. Cloth, $5.00; Half Morocco, $6.50

"It is without doubt the most useful and comprehensive book in the English language on fuels, and is a valuable acquisition to our standard books of reference."—*Journal of the Franklin Institute.*

"It covers a wide range of knowledge, and should be at the elbow of every intelligent and progressive manufacturer."—*The Iron Trade Review, Cleveland.*

"The book will be very useful for reference, and should be of especial value to the inventors and experimenters or users of processes or appliances for the combustion of fuels, since in it can be found a record of a large part of the methods heretofore proposed and adopted. Where critical remarks are made they appear to be judicious. The illustrations are very numerous and are well selected. An immense amount of information has been crowded into these closely printed 802 pages."—*Engineering and Mining Journal, New York.*

"The book is very fully illustrated, as, indeed, the nature of the subject requires, and includes a large number of tables giving fuel statistics, analyses of different fuels, and comparative results."—*The Railroad and Engineering Journal.*

Vol. II. **Lighting.** Candles, Oils, Lamps, etc. By W. Y. DENT, I. MCARTHUR, L. FIELD, F. A. FIELD, BOVERTON REDWOOD, and D. A. LOUIS. 358 Illustrations. Octavo.
Cloth, $4.00; Half Morocco, $5.50

Vol. III. **Gas Lighting.** By CHARLES HUNT, Manager of the Birmingham Corporation Gasworks. Illustrated. Octavo.
Cloth, $3.50; Half Morocco, $4.50

Vol. IV. **Electric Lighting.** *Preparing.*

GARDNER. The Brewer, Distiller, and Wine Manufacturer. Giving full Directions for the Manufacture of Beers, Spirits, Wines, Liquors, etc., etc. A Handbook for all interested in the manufacture and sale of Alcohol and Its Compounds. Edited by JOHN GARDNER, F.C.S., Editor of "Cooley's Cyclopedia" and "Beasley's Druggists' Receipt Book." Illustrated. Cloth, $1.50

"Trustworthy and valuable."—*German and American Brewers' Journal.*

"A very complete handbook."—*Boston Journal of Chemistry.*

Bleaching, Dyeing, and Calico Printing. With Formulæ; a Chapter on Dye Stuffs. Illustrated. 12mo. Cloth, $1.50

"A serviceable manual."—*Inventors' and Manufacturers' Gazette.*

CAMERON. Oils and Varnishes. A Practical Handbook, by JAMES CAMERON, F.I.C. With Illustrations, Formulæ, Tables, etc. 12mo. Cloth, $2.25

Soap and Candles. A New Handbook for Manufacturers, Chemists, Analysts, etc. 54 Illustrations. 12mo. Cloth, $2.00

EMERGENCIES.

DULLES. Accidents and Emergencies. A Manual for the Treatment of Surgical and other Injuries, Poisoning and various Domestic Emergencies, in the absence of the Physician. By CHARLES W. DULLES, M.D., Surgeon to the Out-Door Department of the University and Presbyterian Hospitals, Philadelphia. Fifth Edition, Enlarged. New Illustrations. 12mo. Cloth, $1.00

"This is a revised and enlarged edition, with new illustrations, of the manual, explaining the treatment of surgical and other injuries in the absence of the physician. The simple and practical suggestions of this little book should be known to every one. Accidents are constantly occurring, and a knowledge of what should be done in an emergency is very valuable. Such a handbook should be in every home, placed where it can always be found readily."—*Boston Journal of Education.*

WATER AND MILK ANALYSES.

LEFFMANN. Examination of Water for Sanitary and Technical Purposes. Presenting those Processes that are Most Trustworthy and Practical. By HENRY LEFFMANN, M.D., Professor of Chemistry and Metallurgy, Pennsylvania College of Dental Surgery; Professor of Chemistry, Woman's Medical College of Pennsylvania, etc. Fourth Edition. Revised and Enlarged. Illustrated. 12mo. Cloth, $1.25

"This is a well-compiled and useful little treatise."—*London Lancet.*

"An admirable digest of our present knowledge."—*Journal of Analytical Chemistry.*

"Especially valuable is the section on interpretation of results."—*Railroad and Engineering News.*

BY THE SAME AUTHOR.

Analysis of Milk and Milk Products. Arranged to suit the needs of Analytical Chemists, Dairymen, and Milk Inspectors. Second Edition. Enlarged. 12mo. Cloth, $1.25

"The book is one which will be useful in the hand of the dairyman, as well as in the hands of those whose duty it is to see that he deals fairly with his customers."—*London Sanitary Record.*

CARPENTER. The Microscope and Its Revelations. By W. B. CARPENTER, M D , F R S. Eighth Edition. By REV. DR. DALLINGER, F R S. Revised and Enlarged, with 800 Illustrations and 21 Lithographs. Octavo. 1100 pages. *Preparing.*

"The book, therefore, cannot fail to be of value to chemists and others at iron works intrusted with the microscopical examination of the metals with which they deal."—*The American Manufacturer, Pittsburgh.*

"Every one who has a microscope will need also Carpenter's book to get the most out of his instrument, and every one who has the book will be certain to want a microscope."—*Popular Science Monthly.*

"It is without a rival in its particular field, and is beyond question the best single work on the subject, not only in English but in any other language. . . . A splendid specimen of the book-maker's art."

"The book is more than ever a standard, unrivaled in its kind, and is a necessity to every one who pretends to any scientific use of the microscope."—*New York Evening Post.*

WETHERED. Medical Microscopy. By FRANK J. WETHERED, M.D., M.R.C.P. With 100 Illustrations. 12mo. Cloth, $2.00

REEVES. Medical Microscopy. Including chapters on Bacteriology, Neoplasms, Urinary Examination, etc. By JAMES E. REEVES, M.D., Ex-President American Public Health Association, etc. Illustrated. 12mo. Cloth, $2.50

THE BEST DICTIONARY.

GOULD. Illustrated Dictionary of Medicine and Allied Sciences, including Chemistry, Biology (Zoology and Botany), Hygiene, etc. Large, Square Octavo. 1633 pages.

Half Morocco, } $10.00. With Thumb Index, $11.00
Full Sheep, }
Fifth Edition. Half Russia, Thumb Index, $12.00

⁂ There being no special dictionaries devoted to **Chemistry and Biology,** it was thought eminently proper to include both these sciences in this book. They are closely related to medicine, and each is largely dependent upon the others. Gould's Illustrated Dictionary contains much special information of practical use to the general scientist. **Bacteriology and Parasitology** are particularly well presented, while the **numerous tables** of Acids, Alcohols, Aldehyds, Carbohydrates, Electric Units, Ethers, Foods, Hydrocarbons, Laws, Milks, Oils, Pigments, Ptomains, Resins, Soaps, Stains, Starches, Sugars, Tests, Theories, Wave Lengths, Weights and Measures, etc., will be found unique and exceedingly valuable.

☞ Handsome descriptive circular, with sample pages and illustrations, will be sent free upon application. 100,000 copies of Gould's Dictionaries have been sold.

NOTTER and FIRTH. The Theory and Practice of Hygiene. A Complete Treatise by J. LANE NOTTER, M.A., M.D., F.C.S., Fellow and Member of Council of the Sanitary Institute of Great Britain; Professor of Hygiene, Army Medical School; Examiner in Hygiene, University of Cambridge, etc., and R. H. FIRTH, F.R.C.S., Assistant Professor of Hygiene, Army Medical School, Netly. Illustrated by 10 Lithographic Plates and 135 other Illustrations, and including many Useful Tables. Second Edition, Carefully Revised. Octavo. *In Press.*

*** The standard authority in the United States and British Army and Navy.

PARKES. Hygiene and Public Health. A Practical Manual. By LOUIS C. PARKES, M.D., D.P.H., London Hospital; Assistant Professor of Hygiene and Public Health at University College, etc. Fifth Edition, Enlarged and Revised. 80 Illustrations. 12mo. Cloth, $2.50

"Dr. Parkes' experience as a teacher of public hygiene has enabled him to deal with the whole subject in a practical and intelligible manner."—*The Boston Medical and Surgical Journal.*

STEVENSON AND MURPHY. A Treatise on Hygiene. Illustrated. Edited by THOMAS STEVENSON, M.D., F.R.C.P., Lecturer on Chemistry and on Medical Jurisprudence at Guy's Hospital, Official Analyst to the Home Office; and SHIRLEY F. MURPHY, Medical Officer of Health to the County of London.

Vol. I.	9 Plates.	186 Illustrations.	1013 pages.	Cloth, $6.00
Vol. II.	45 Plates.	31 Illustrations.	847 pages.	Cloth, $6.00
Vol. III.	Sanitary Law.		459 pages.	Cloth, $5.00

EACH VOLUME SOLD SEPARATELY.

"The different topics are fully and intelligently treated, especially those which relate to the subjects of Ventilation, Water, Soil, Food, Physical Education, the Dwelling, and the Disposal of Refuse. The work is fully illustrated with plates, diagrams, and wood-cuts, and pains appear to have been taken to bring the information upon each topic up to date."—*The Boston Medical and Surgical Journal.*

"All the topics are treated with a thoroughness of detail leaving nothing to be desired. The contents are valuable alike to the physician, the municipal health officer, and the sanitary engineer."—*Medical Record, New York.*

KENWOOD. Public Health Laboratory Work. By H. R. KENWOOD, M.B., D.P.H., F.C.S., Instructor in Hygienic Laboratory, University College; late Assistant Examiner in Hygiene, Science and Art Department, South Kensington, London, etc. With 116 Illustrations and 3 Plates. Cloth, $2.00

***** For complete list of books on Hygiene, send for our Special Catalogue.**

THE PRICES OF THESE BOOKS ARE NET.

83–95 Oct 20–22
95–109 " 22–25
109–119 " 27–29
91–119 (written) } " 29–Nov 1